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# Interim Report on the Feasibility of Using UV (Ultraviolet) Photolysis and APEG (Alkali Polyethylene glycolate) Reagent for Treatment of Dioxin Contaminated Soils

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# INTERIM REPORT ON THE FEASIBILITY OF USING U.V. PHOTOLYSIS AND APEG REAGENT FOR TREATMENT OF DIOXIN CONTAMINATED SOILS

by

James B. White
Keith E. Leese
Andy C. Clayton

Research Triangle Institute
P. O. Box 12194
Research Triangle Park, NC 27709

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Project Officer:

Charles Rogers

U.S. Environmental Protection Agency
Chemical and Biological Detoxification Branch
Hazardous Waste Engineering Research Laboratory
Cincinnati, Ohio 45268

HAZARDOUS WASTE ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OH 45268

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16. ABSTRACT

Alkali polyethylene glycolate (APEG) was field tested at Shenandoah Stables in Moscow Mills, Missouri, to evalute the chemical's potential to dechlorinate 2,3,7,8-tetrachlorodibenzo-p-dioxin [2,3,7,8-TCDD] under field conditions.

An experimental design employing a Latin square was used to compare five levels of treatments. The treatments were designated: (1) APEG-treated and covered, (2) APEG-treated and uncovered, (3) not treated and covered, (4) not treated and uncovered, and (5) methoxpolyethylene glycol (MPEG) control and uncovered. In addition to the arena site, two sections of bleachers were also treated with APEG to determine the chemical's ability to decontaminate dust-covered surfaces.

It was determined that there was not a statistical difference between those plots treated with APEG and those treated with the MPEG control. Soil moisture was determined to be on the order of 18 to 21 percent by water weight. APEG has been determined to be extremely hygroscopic. This property resulted in its deactivation and prevented significant TCDD reduction in the Latin square experiment. The bleachers test showed approximately a 32-percent and a 16-percent reduction in 2,3,7,8-TCDD in the final dust samples after a single application of APEG.


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## FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small businesses in handling their wastes responsibly and economically.

This report describes a contained field application of an alkaline polyethylene glycol reagent (APEG) for the in-situ dehalogenation of chlorodioxin (TCDD) contaminated soils in Missouri. It will be useful to EPA's Office of Solid Waste (OSW).

For further information, please contact the Alternative Technologies Division of the Hazardous Waste Engineering Research Laboratory.

David G. Stephan, Director
Hazardous Waste Engineering Research Laboratory

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## EXECUTIVE SUMMARY

In 1982, numerous sites of 2,3,7,8-tetrachlorodibenzo-p-dioxin (dioxin, 2,3,7,8-TCDD) contamination were identified by the U. S. Environmental Protection Agency (EPA) in Eastern Missouri. The sites were contaminated in the early 1970's when waste oil containing traces of dioxin were applied to horse arenas and road surfaces for the purposes of dust control. Due to the number of sites and the volume of soil that must be handled, it is possible that in situ treatment may provide the only practical solution to the dioxin problem.

The Hazardous Waste Engineering Research Laboratory (HWERL-Ci), in conjunction with Wright State University, in Dayton, Ohio, previously established the ability of alkali polyethyleneglycolates (APEG's) to destroy 2,3,7,8-TCDD in soil samples under laboratory conditions. Subsequently, EPA developed plans to evaluate the applicability of APEG's to dioxin decontamination in a controlled field test.

The objective of this study was to evaluate a selected APEG reagent and ultraviolet light (UV) under ambient conditions to determine its capability to dechlorinate and hence "destroy" 2,3,7,8-TCDD. The objective was to be accomplished through the use of a statistical sampling design that would facilitate the comparison of results before and after treatment. Using this approach, data essential to the developm of a reliable and cost-effective technique for the destruction and/or detoxification of toxic halogenated organics, such as TCDD, would be obtained.

EPA, in conjunction with the Research Triangle Institute (RTI), implemented the statistical design in a field study conducted at Shenandoah Stables in October through November 1984.

The test plan involved the construction of two sites, one inside the stable arena and one outside the stable at a site referred to as the "slough".

The slough area immediately southeast of the stable was the location where 1,060 cubic yards of TCDD contaminated soil were removed from the stable, deposited in the area, and capped with clay in the 1970's. The TCDD concentration in this area averaged 1,175 ppb. On the 25 test plots inside the arena the TCDD concentration averaged 110 ppb.

Extremely wet weather forced the postponement of the outside UV and APEG tests until the summer of 1985.

The basic experimental design for the Shenandoah Stable site consisted of a 5 x 5 Latin square involving 25 plots (identified by row and column). The five treatments, designated by the letters A through E as shown below, were randomly assigned within the Latin square configuration:

- A = APEG treated, covered
- B = Not treated, covered
- C = APEG treated, uncovered
- D = Not treated, uncovered
- E = Methyoxypolyethylene glycol (MPEG)-treated, uncovered

Two sections of bleachers were identified that were liberally coated with dust were identified. Each section contained two seating planks that were 31.5-feet long and 9.6-feet wide, and arranged in tiers. The planks were coated with dust ranging in depth from 1/16 inch to 1/8 inch. It was assumed that since all four planks had been exposed to the same environment, each would contain approximately the same levels of 2,3,7,8-TCDD. Therefore, one plank of each set could be treated with APEG in order to determine the APEG's ability to decontaminate dust-covered surfaces.

Treatment of the 3-foot by 3-foot test plots involved the application of APEG and MPEG (polyethylene glycol monomethyl ether, average molecular weight 350) to designated plots, followed by a plastic covering placed over the

appropriate plots. To prepare the APEG reagent, the MPEG was combined with potassium hydroxide and also used alone as a reagent control.

The plots designated A and C (Figure I) were given a single treatment of APEG. The initial treatment consisted of filling a 2-gallon steel watering can having a perforated spray cap with 7-liters of APEG. The reagent was then dispersed over the surface of a plot and allowed to fill the frame. The surface of the treated plots was then raked and stirred to a depth of approximately 3 inches with a 3-pronged garden tool in order to mix the APEG and the soil. Those plots designated as E received a similar treatment using 7 liters of MPEG. Plots designated as B and D were left untreated; however, their surfaces were raked to simulate the mixing that had occurred in A, C, and E.

The plots designated by A and B were covered with 0.5 mm black polyethylene plastic. A 3 1/2-foot, 1-inch by 1-inch dowel was centered horizontally over the sampling frame to provide central elevation for the covering and to promote the drainage of condensate to the sides of the plot. The 5-foot by 5 foot plastic squares were then placed over the frame.

Additional treatments involved the application of a 2 to 1 toluene-APEG mixture to those sites previously treated with APEG alone. The MPEG treatments were not modified.

The previously identified bleacher sections are treated during the third visit. A standard 3-gallon hand-pressurized agricultural sprayer was used to apply the APEG. The sprayer was filled with a 2 to 1 toluene-APEG mixture and the spray nozzle was tested to see that it would emit a uniform spray.

After adjusting the spray nozzle, the can was refilled and two 31-foot by 9.6-foot (302.4 square feet) planks of bleacher were each sprayed with approximately 1 1/2 gallons of APEG reagent each.

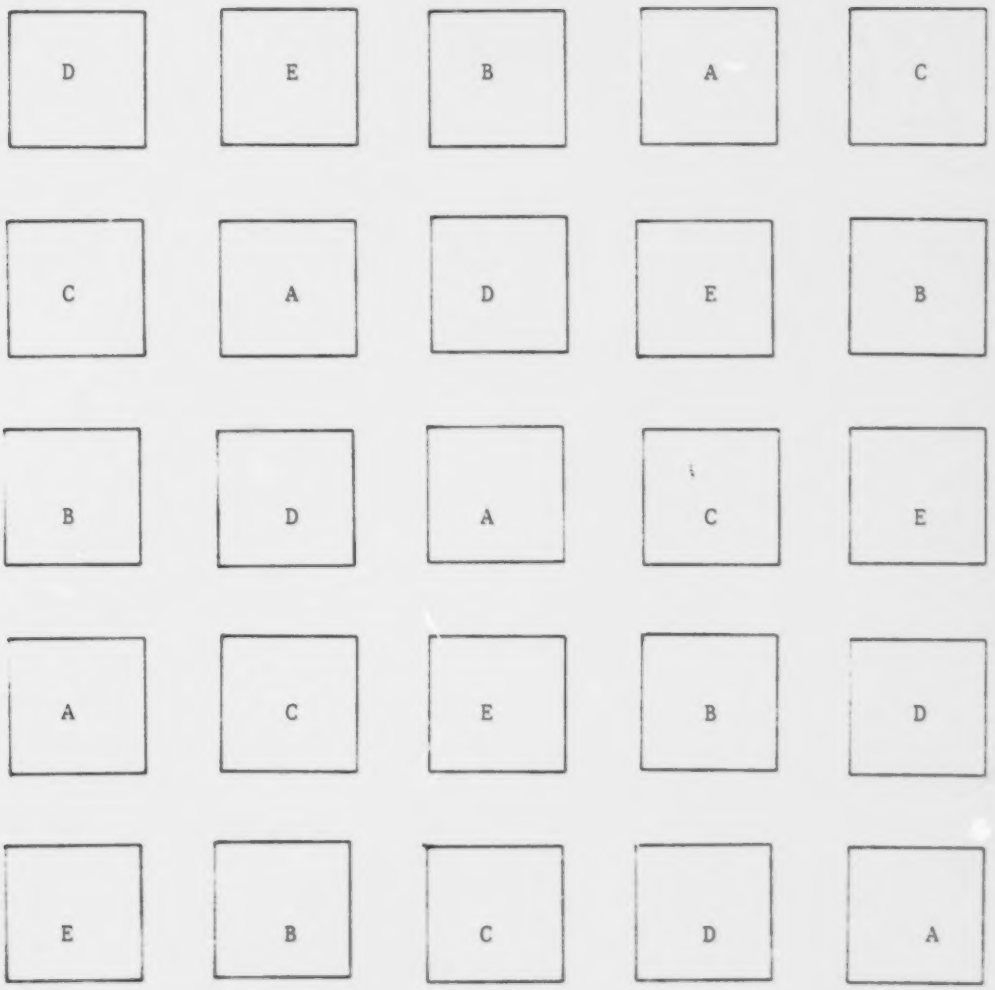



Figure I. Plot assignments for the arena site.

The concentration of 2,3,7,8-TCDD at Shenandoah Stables had been previously determined by EPA to have a nonuniform distribution. Consequently, the goal of the sampling protocol was to provide a characterization of each plot over time that would account for the potential variability. It was determined that by compositing a series of point samples from within each plot, they could be analyzed to determine a representative 2,3,7,8-TCDD concentration. The sample points were based on a regular pattern, the starting point of which was to be randomly selected for each sample.

The analyses of the soil and bleacher samples for 2,3,7,8-TCDD was performed under the auspices of the Superfund National Dioxin Study. Consequently, four contract laboratories were assigned by the Sample Management Office, in Alexandria, Virginia, to perform the TCDD analysis. All analyses were performed in accordance with the established EPA TCDD analysis protocol requirements for laboratories the study.

Duplicate measurements of dioxin concentration levels within each of the plots were made at four times: the first pair of measurements during a baseline period (prior to application of any treatment), and the remaining pairs, after each of the three treatment applications. A total of 200 measurements (2 measurements per plot; 25 plots; 4 time periods) were finally taken. Due to miscommunictiaons between the Sample Management Office and the contract laboratories, all samples results were not received. Consequently, there were 31 measurements for which the dioxin concentrations were not available for analysis. However, each of 100 cells (25 plots, 4 time periods) had at least one good dioxin determination.

A multivariate analysis of variance was performed on the sample data using the dioxin data from the four sampling visits and looking at them over

time as the dependent variables and looking at row, column, and treatment as the independent variables.

Upon inspection of only the initial measurement versus the final measurements (Figure II) there is an effect for APEG versus no treatment as well as MPEG versus no treatment. When comparing the effect of the no treatment "treatments," both show a statistically significant increase in dioxin levels. The effect of the MPEG and APEG treatments show a decrease in dioxin levels but are not statistically significant.

The results from one application of APEG to TCDD contaminated bleachers are summarized in Table I.

The results from field tests of APEG are not comparable to the achieved 68 percent reduction of TCDD in soil after 21 days under ambient conditions in the laboratory. A recently completed study has established that both APEG and MPEG are hygroscopic and can absorb within 9 days greater than 10 percent of its weight in moisture from the air. Moisture in excess of four percent tends to deactivate the APEG reagents and reduce their ability to destroy TCDD and other haloorganic compounds.

TABLE I. PERCENT REDUCTION OF TCDD ON BLEACHER SURFACES

| Shenandoah Stable bleacher dust | | |
|---|---|---|
| Initial TCDD in dust (PPB) | TCDD after 12 days of treatment | Percent reduction |
| 76.9 | 64.0 | 16.8 |
| 65.5 | 44.0 | 32.8 |

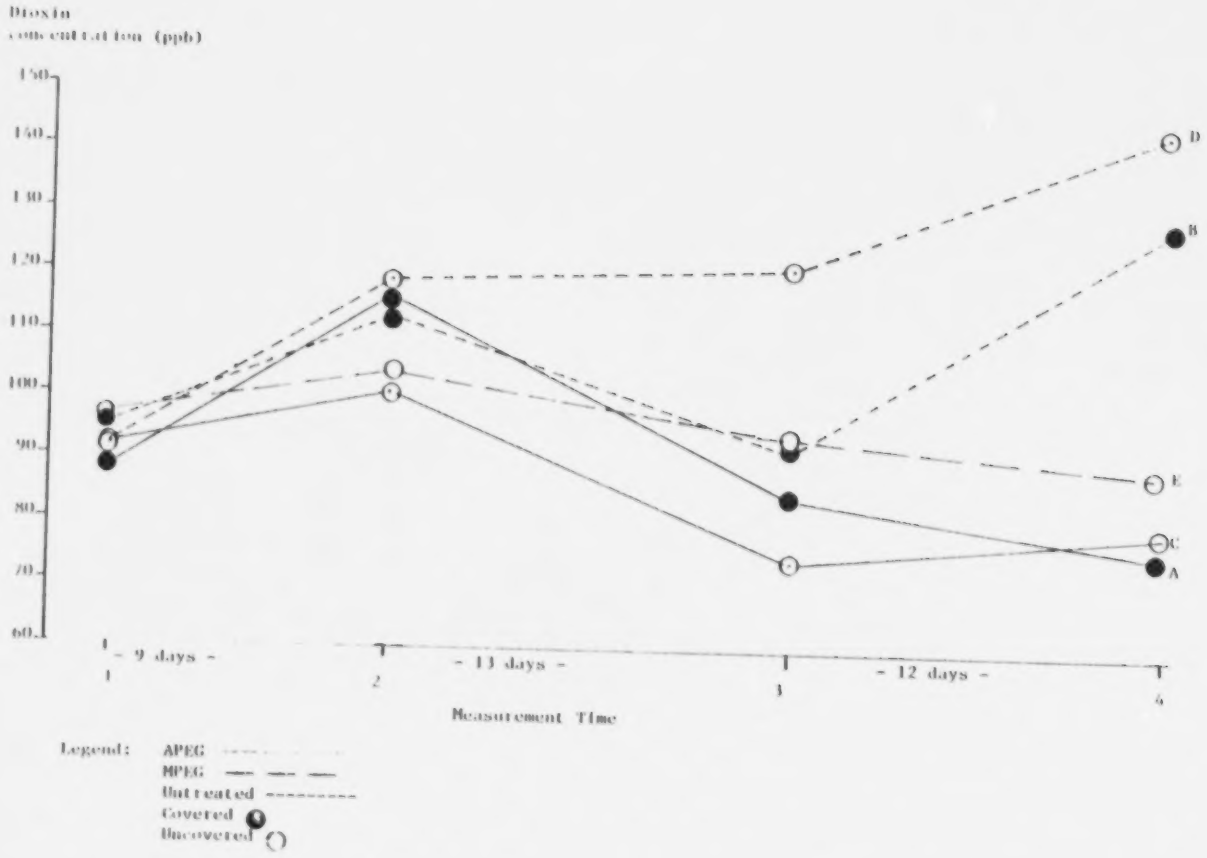



Figure II. Estimated mean dioxin concentrations versus measurement time.

Soil moisture in test plots at Shenandoah Stables reached levels of 18 to 20 percent of the weight of the soil during the study. Also, the humidity remained high due to an unseasonable amount of heavy rainfall during the test period of October through November 1984, the average air temperature at the test site was 35°F. This low temperature did not contribute to drying of soil, nor could it enhance the APEG rate of TCDD destruction in the soil or on the bleacher planks.

To overcome the adverse influence of soil and air moisture on APEG, two new TCDD destruction processes are being developed and demonstrated successfully on the laboratory scale. They are heated slurry and heated in situ processes.

In the slurry process the TCDD-contaminated soil is excavated and placed in an onsite reactor containing APEG. The soil is processed for 1 hour at 70° to 100°C to decompose the dioxin to levels below 1 ppb. The APEG is recovered and reused. In the in situ process the soil is treated in-place by adding the reagent directly to the soil as was done at the Shenandoah site, followed by heating the soil to 70°C with radio frequency or passive solar techniques. Both the heated slurry and heated in situ processes are scheduled to be tested in the field during FY85-86.

## ABSTRACT

Alkali polyethylene glycolate (APEG) was field tested at Shenandoah Stables in Moscow Mills, Missouri, to evaluate the chemical's potential to dechlorinate 2,3,7,8-tetrachlorodibenzo-p-dioxin [2,3,7,8-TCDD] under field conditions. Two tests were scheduled for the early summer 1984, one inside the stable arena and the other outside in an area known as the "slough." However, access to the site was delayed until the fall of 1984 due to difficulties in obtaining the owner's approval. Because of extremely wet weather during the fall, the outside test was postponed until the summer of 1985.

An experimental design employing a Latin square was used to compare five levels of treatments. The treatments were designated: (1) APEG-treated and covered, (2) APEG-treated and uncovered, (3) not treated and covered, (4) not treated and uncovered, and (5) methoxpolyethylene glycol (MPEG) control and uncovered. In addition to the arena site, two sections of bleachers were also tested with APEG to determine the chemical's ability to decontaminate dust-covered surfaces.

An analysis of variance was performed on the sample data. It was determined that there was not a statistical difference between those plots treated with APEG and those treated with the MPEG control. The deactivation of APEG was directly attributable to the fact that APEG is moisture-sensitive. In addition to the general humidity produced by the continual rainfall during the project, there was a presence of high soil moisture inside the stable. This soil moisture was determined to be on the order of 18 to 21 percent by water weight. The APEG has since been determined to be extremely hygroscopic and capable of pulling moisture from out of the surrounding environment resulting in its deactivation. The bleachers test showed approximately a 32-percent and a 16-percent reduction in 2,3,7,8-TCDD in the final dust samples after a single application of APEG.

# SECTION 1

# INTRODUCTION

In 1982, numerous sites of 2,3,7,8-tetrachlorodibenzo-p-dioxin (dioxin, 2,3,7,8-TCDD) contamination were identified by the U.S. Environmental Protection Agency (EPA) in Eastern Missouri. The sites were contaminated in the early 1970's when waste oil containing traces of dioxin were applied to horse arena surfaces and road surfaces for the purposes of dust control. Due to the number of sites and the volume of soil that must be handled, it is possible that in situ treatment may provide the only practical solution to the dioxin problem.

The Hazardous Waste Engineering Research Laboratory (HWERL), in conjunction with Wright State University, Dayton, Ohio previously established the ability of alkali polyethyleneglycolates (APEG's) to destroy 2,3,7,8-TCDD in laboratory tested soil samples. Subsequently, EPA developed a plan to evaluate the applicability of APEG's to dioxin decontamination in a controlled field test.

The objective of this study was to evaluate a selected APEG reagent and ultraviolet light under ambient conditions to determine its capability to dechlorinate and hence "destroy" 2,3,7,8-TCDD. The objective was to be accomplished through the use of a statistical sampling design that would facilitate the comparison of results before and after treatment. Using this approach, data essential to the development of a reliable and cost effective technique for the destruction and/or detoxification of toxic halogenated organics, such as TCDD, would be obtained.

The Research Triangle Institute (RTI) was contracted by HWERL to implement the statistical design in a field study to be conducted at Shenandoah Stables. In late September, 1984, RTI, with the capable assistance of O.H. Materials, Inc., in St. Peters, Missouri, began work. The test plan involved the construction of two sites, one inside the stable arena, the second outside the stable at a site referred to as the "slough." Each site was to consist of 25 plots arranged in a 5 by 5 Latin square.

Extremely wet weather during the fall of 1984 forced the postponement of the outside APEG/U.V. tests until the following summer. However, the inside tests were carried through to completion. The data obtained from those plots and additional sites in the bleacher area of the arena that were designated to test APEG in the decontamination of ambient dust-covered surfaces are the subject of this report.

## SECTION 2

## SUMMARY, CONCLUSIONS and RECOMMENDATIONS

This section provides a general summary of the statistical analysis contained in Section 7, Statistical Analysis Results, the results of bleacher decontamination, and recommendations for future activities. In addition, certain unexpected increases in dioxin levels are rationalized.

### 2.1 SUMMARY

"Treatments" were randomly assigned to the individual plots in a Latin square design. Initial baseline samples were taken and the treatments were applied. Approximately 2 weeks later, two samples were taken from each plot and the assigned treatments (the same treatment to the same plots) were again applied. The sample and treatment protocol was repeated 4 times (2 samples per plot; 25 plots; 4 time periods) so that a total of 20 samples were taken. There were 31 samples for which the dioxin concentrations were not available for analysis. However, each of 100 cells (25 plots, 4 time periods) had at least one good dioxin determination.

In the typical analysis of a Latin square design there is only one measurement per cell and, therefore, the row column, row treatment, and column treatment interaction are assumed to be nonsignificant. These interactions can confound the tests for main effects for row, column, and treatment. Therefore, the use of multiple observations per cell made it possible to test for these interactions. These tests were performed on the baseline data only and the new column, row treatment, and column treatment interactions were found to be nonsignificant.

### 2.2 CONCLUSIONS

A multivariate analysis of variance (ANOVA) was performed on the sample data using the dioxin data from the four sample visits and looking at them

over time as the dependent variables and using row, column, and treatment as the independent variables. The main effects test for both row and column resulted in nonsignificant differences. The main effects test for treatment was significant with p value = .016.

The simple main effect tests for treatment were evaluated at different times using a p value of 0.10. There are statistically significant differences in tests from Time 1 to Time 4 and from Time 2 to Time 4. A pair-wise comparison of sample means for the increase in dioxin leavels from Time 1 to Time 4 and from Time 2 to Time 4, respectively, was made. The APEG, uncovered, minus no treatment; uncovered, gives a difference of 46.4 ppb but is not statistically different from zero. This does not mean that these two treatments are not different, only that the data were not accurate enough to determine a difference statistically.

Looking at only the baseline versus the final measurements there is an effect for APEG versus no treatment as well as for methoxypolyethylene glycol (MPEG) versus no treatment. When comparing the effect of the no treatment "treatments", both show a statistically significant increase in dioxin levels but are not statistically significant.

A graph of the dioxin concentration over time shows that dioxin appears to increase in those plots that were not treated and to decrease in those plots that had been treated with the supposedly nonreactive MPEG. These variations are probably indeterminate errors produced by a reliance on the contract laboratories of the National Dioxin Study. These laboratories reported all of their dioxin data on an "as received" or "wet weight" basis. Due to the nature of the dioxin hazard and the brevity of this work, the contract laboratories were unable to dedicate additional space and equipment to generate "dry weight" data.

The inevitable outcome of this lack of dry weight data is that the reported treatment with both MPEG and APEG increased the total proportion of dioxin in the weight of a given sample. Thus, in a given weight of sample, the amount of dioxin proportionately decreased, resulting in an apparent decrease in dioxin that was not attributable to actual destruction or disappearance.

A positive aspect is that the MPEG plot can be used to factor out the weight increase produced through the addition of APEG. The resulting difference is an indication of the actual destructive ability of APEG under the environmental conditions. A comparison of the difference between the MPEG- and APEG-treated plots indicated that they were not statistically different.

The apparent increase in dioxin concentration in the untreated plots is also attributable to the constrained analytical protocol. In each case, there was probably a decrease in the water content of the sample over time resulting in an apparent increase in dioxin. During the first site visit, the soil moisture content was determined using a Speedy Moisture Meter. This apparatus is a pressure vessel in which calcium carbide and soil are mixed. The calcium carbide reacts with the soil moisture to produce acetylene gas. The gas generation can be read on an attached pressure gauge as a pressure increase that can be interpolated from a standard chart in order to determine the soil moisture. The soil moisture was found to range from 18 to 21 percent, which reflected the upper limits of the measuring instrument.

The soil in the untreated plots was raked and exposed to diurnal variation in a temperature of 35°F over a period of 2 months that resulted in a continual drying of the upper 3 inches of soil. Using 21 percent moisture content as a starting point and assuming that the soil can air dry under the ambient conditions to approximately 7 percent moisture, the apparent increase in dioxin produced by the moisture change can be calculated. This calculation produced a

result that was well within the range of the apparent increase. Consequently, it is believed that this is the most likely source of increase.

In addition to the inside test plot, two sections of spectator bleachers were treated with APEG in order to evaluate the chemical's potential for surface decontamination. Each section contained two seating planks, one directly above the other. One plank from each set was swept clean in order to obtain a background dust sample. The second plank of each set was sprayed with APEG from an agricultural hand sprayer, allowed to set for 12 days, and then sampled. The results showed that the 2,3,7,8-TCDD concentrations declined from 76.9 ppb to 64.0 ppb or 16.8 percent in the first set and from 65.5 ppb to 44.0 ppb or 32.8 percent in the second set. No attempt was made to provide a statistical analysis of the bleacher section data.

## 2.3 RECOMMENDATIONS

The field test of APEG did not produce results comparble to the laboratory runs. It is believed that this was due to the deactivation of the APEG reagent by water that was present in the soil and readily available from the surrounding soil reservoir. It is recommended that future work on this site be cognizant of the water problem and that their work be carried out under low moisture conditions. It is important to give consideration to the fact that there will always be relatively high concentrations of moisture in the soil, and consequently, a contained reactor approach might be advisable. This would allow separation of the contaminated soil from the reservoir of soil moisture, facilitate drying, and enhance the APEG reaction.

## SECTION 3

## SITE PREPARATION

Shenandoah Stables, located approximately 30 miles northwest of St. Louis, Missouri, near Moscow Mills, was the proposed site of the test. The test was carried out on two sites, 25 ft by 25 ft, one situated inside the stable arena and the second at an outside site generally referred to as the "slough" area. The actual sites were selected by the EPA HWERL project officer and were laid out under his direction (see Figure 1).

The Shenandoah Stable horse arena became contaminated with dioxin in May 1971 when a St. Louis waste oil hauler sprayed approximately 2,000 gallons of oil on the soil in the arena for dust control. Afterward, numerous birds and rodents and over 40 horses died, and several adults and children became ill.

In August 1971, the top 6 to 8 inches of contaminated soil, approximately 350 cubic yards, were excavated from the arena and used as fill material in a new highway. In April 1972, approximately 18 to 24 inches of soil, 790 to 1,060 cubic yards, was removed from the arena and placed in a slough area immediately southeast of the stables. EPA sampled the site in May and June of 1982. The results indicated that the soil contamination in the arena ranged from 1 to 127 parts per billion (ppb) in the top 30 inches of the soil. In addition, dust taken from the spectator bleachers contained 110 ppb of dioxin. [1]

### 3.1. SLOUGH AREA

The HWERL project officer directed the staking out of a plot in the slough area and designated a spoils area. The underbrush was removed from the site and stacked at a preselected site. An attempt was made to remove the top layer of soil by hand in order to expose the original soil. It was anticipated that this would require the removal of at least the top 6 inches of a clay overburden; however, the overburden actually ranged in depth from 12 to 18 inches and was densely packed.

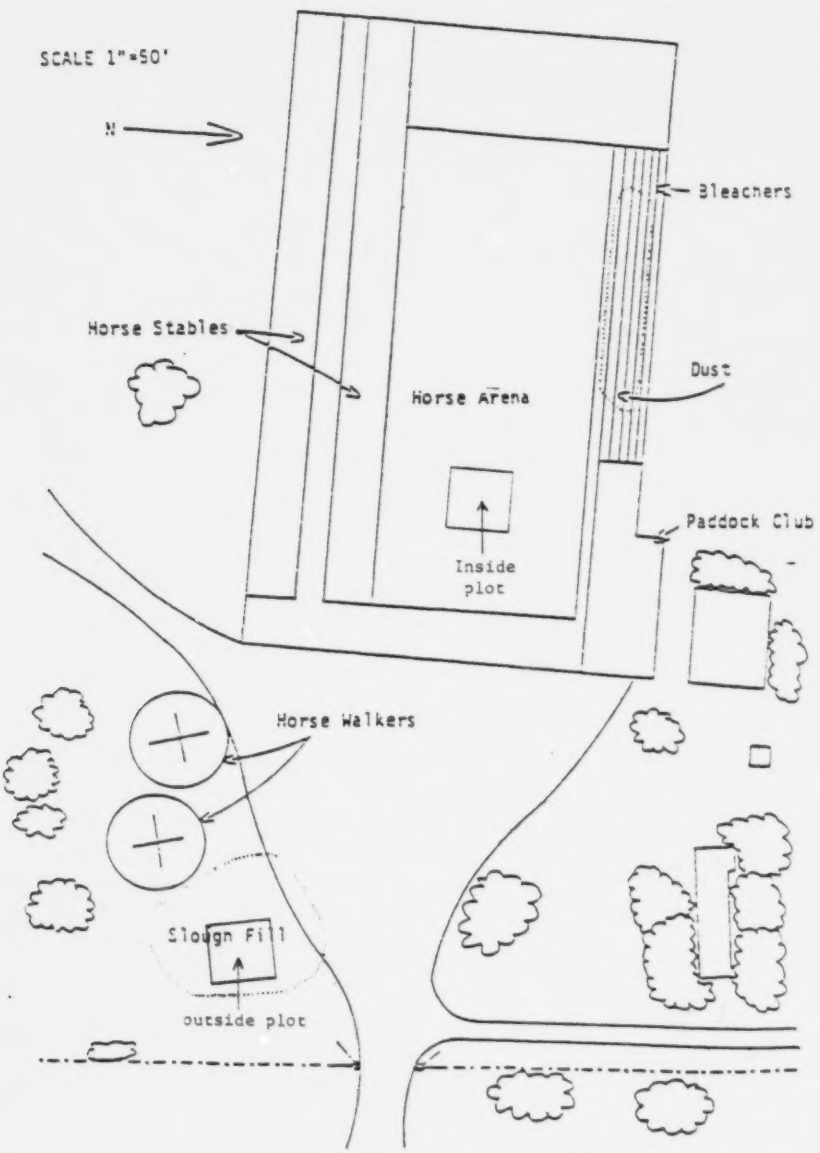



Figure 1. Location of test plots at Shenandoah Stables.

It was necessary to move the site approximately 10 feet further west and to use a Rototiller to break up the clay cap. This attempt was time consuming and therefore impossible to complete on the first day. The soil that was removed was placed around the periphery of the site to form a berm to protect the area from possible runoff from adjacent areas caused by rainfall. In addition, a 5 mil clear polyethylene plastic cover was placed over the site to protect it overnight. During the night rain occurred and water penetrated the protective cover. Due to the muddy conditions that resulted, it was necessary to suspend the excavations until more favorable conditions were present. The wet weather continued over the next few weeks, making it necessary to postpone the outside operations until the following summer (see Appendix A).

## 3.2 ARENA SITE

The HWERL project officer also designated a plot inside the stable arena. This site was approximately 35 feet by 25 feet and consisted of a hard-packed surface laced with cracks that were approximately 1/2- to 1-inch deep. The cracks were apparently produced by the desiccation of the upper soil layer.

The site was cleared of debris and Rototilled to a depth of approximately 6 inches. The area was repeatedly worked until the soil was relatively uniform in consistency. It was then raked to remove any dirt clods greater than 2 inches in diameter and to provide a relatively flat surface for the placement of the sampling frames.

### 3.2.1 Arena Plot Layout

The designated arena area was sectioned into a latin square consisting of 25 plots, each one 3 ft by 3 ft square; 5 plots per row and 5 plots per column, separated by 2 feet of walkway. The 25 plots covered a total 529 square feet. The sections formed a grid pattern marked by wooden stakes and nylon cord. The base of the grid was assigned to the edge of the Latin square nearest to the front door of the stable; the top of the grid faced the rear of the stables.

Sampling frames consisting of open-ended boxes, 3 ft by 3 ft and made from 1 inch by 6 inch wood stock, were placed on the grid. They were packed into the soil to a depth of 3 inches, as measured by a standard 12-inch ruler, and were leveled on all sides using a standard 4-foot carpenter's level.

TABLE 1. TREATMENT ASSIGNMENTS

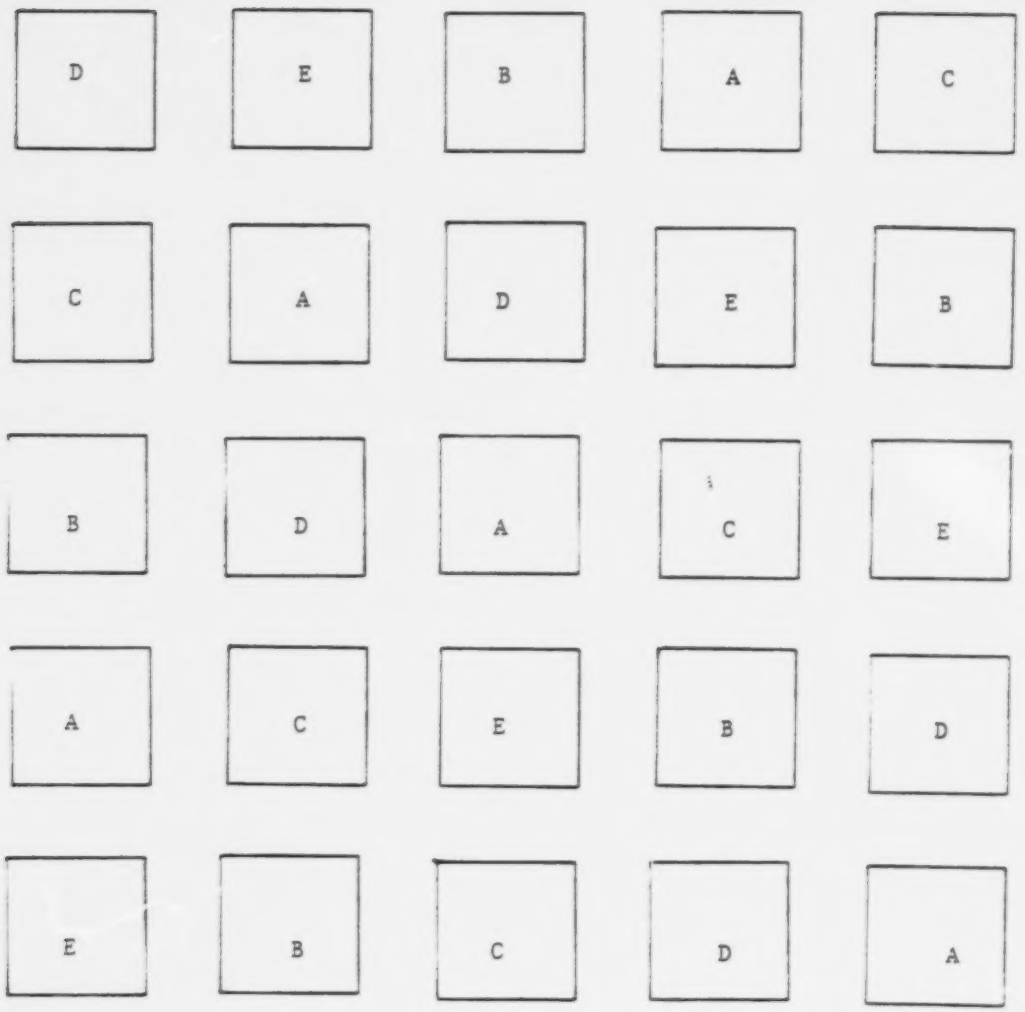
| Treatment label | Assigned treatment |
|---|---|
| A | Treated with APEG, covered |
| B | Untreated, covered |
| C | Treated with APEG, uncovered |
| D | Untreated, uncovered |
| E | Treated with MPEG, uncovered |

The sampling frames were then designated with the letters A, B, C, D, or E written with a magic marker in two places on the side of each frame (see Figure 2). The letters correspond to a predetermined random sequence of assigned treatments (see Table 1).

3.3 BLEACHER SELECTION

Two sections of a bleacher liberally coated with dust were identified. The bleacher had seating planks that were 31.5-feet long and 9.6-feet wide that were arranged in tiers. Two sections of bleacher, coated with dust ranging in depth from 1/16 inch to 1/8 inch, were selected. Each section contained two seating planks, one directly above the other. It was assumed that since both sections had been exposed to the same environment, each would contain approximately the same levels of 2,3,7,8-TCDD. Therefore, one plank from each set could be sampled for a background reading and the second of each set could be treated with APEG in order to determine the chemical's ability to decontaminate dust surfaces.

Rear of stable (+): Top of site




Front of stable (↓): Bottom of site

Figure 2. Plot assignments for the arena site.

## SECTION 4

## SAMPLING PROTOCOL

The concentration of 2,3,7,8-TCDD at Shenandoah Stables had been previously determined by EPA to have a nonuniform distribution. Consequently, the goal of this sampling protocol was to provide a characterization of each plot over time that would account for the potential variability. It was determined by RTI that this could best be done by compositing a series of point samples from within each plot in order to determine a representative 2,3,7,8-TCDD concentration. The sample points were to be based on a regular pattern, the starting point of which was to be randomly selected for each sample.

### 4.1 DETERMINATION OF SAMPLE POINTS

An imaginary uniform grid pattern was mapped out over the surface of each plot. The starting point for each grid was predetermined by the coordinates selected at random from a number sequence corresponding to ½-inch intervals on a 36-inch ruler, e.g., 6, 10. These coordinates were plotted on a Cartesian coordinate system corresponding to the edge of the sample frame (see Figure 3). The coordinate lines had a common origin corresponding to the bottom left corner of each frame.

The randomly selected starting points were marked off on each coordinate axis and a grid was constructed using tic marks at 6-inch intervals to the right and left of each starting point. Two rigid straightedge steel rulers were placed horizontally on the top edge of the frame so as to intersect with each other at right angles. They were aligned with the first grid mark beginning at the lower-most left corner of the frame. The angle formed in the top right quadrant of the intersection designated the sample point.

Samples were taken using JMC "O" Contamination Coring Tubes purchased from JMC Company in Indiana. The coring tubes were of two types, stainless steel and acetate. Each was conspicuously marked 6 inches from the bottom on

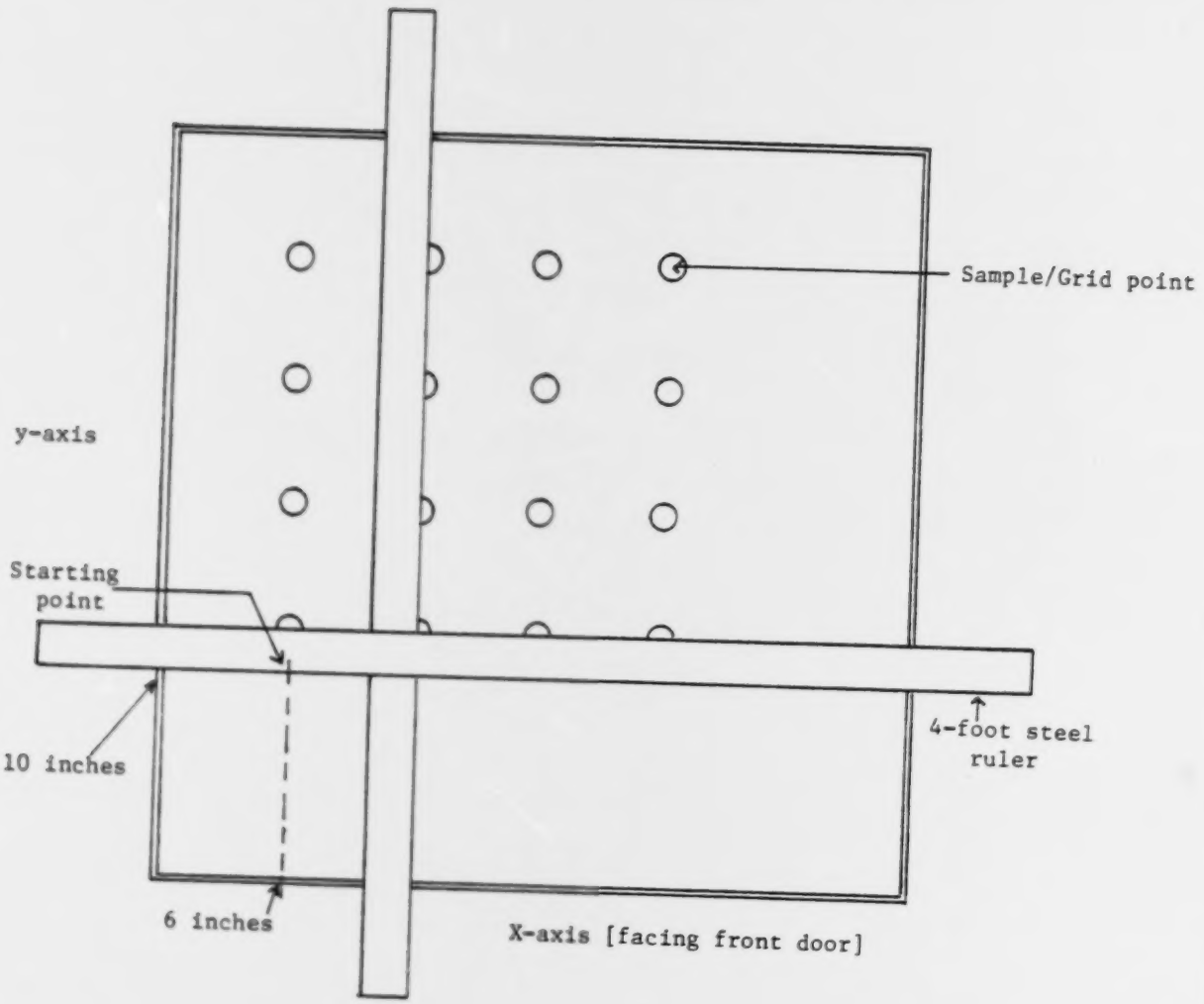



Figure 3. Typical plot showing sample grid.

the barrel. This compensated for 3 inches of soil penetration and 3 inches of clearance between the soil and the top edge of the sample frame. This technique allowed a uniform penetration of the soil surface with respect to a predetermined point. This minimized the inclusion of soil that had not been characterized for dioxin therefore reducing any effect of soil subsidence over time.

Using this method, 16 core samples were collected per plot. Each core was approximately 0.8 inches in diameter and 2 1/2- to 3-inches long. The cores were removed from the coring tubes and composited in EPA QA/QC certified glass sample bottles obtained from the Superfund Sample Bottle Repository in Haywood, California. Upon collection of the 16th sample, the containers were sealed and taken to a collection point adjacent to the site for further handling. In order to obtain a statistically valid sample it was essential to repeat the procedure for each plot prior to treatment. This yielded a total of 2 samples per plot, 50 samples per test area, and 100 samples total per visit per site.

## 4.2 SAMPLE HANDLING

The main areas of concern regarding the soil samples collected for this project included: (1) the choice of the proper sample containers to prevent sample deterioration, (2) prevention of exposure of personnel and the environment to possibly contaminated material, and (3) proper documentation of all phases of sample handling.

The soil samples were collected in wide-mouth glass jars, 32 ounce in size. These bottles were acquired through the Super Fund Sample Bottle Repository. The bottles were QA certified clear glass jars with tight screw-on lids that were lined with Teflon-baked poly caps. All contact of the sample with plastic or paper liners was avoided.

During sample handling, exposure of personnel and the environment outside of the immediate sampled area was avoided by conducting the container-filling and the compositing at the sample site. Sample contact with the outside of the container was minimized by securing a plastic bag around each glass bottle with a rubber band and securing an additional plastic bag around the lid prior to bringing the bottles on to the arena site.

The bottles were filled and stored in their original cartons (12 bottles per carton) at a designated site adjacent to the work area. Upon completion of the sampling effort and prior to treatment, the cartons were carried outside

the site to a designated transfer point inside the stable perimeter fence. There, the boxes were unpacked and the bottles were passed over the fence to personnel of O.H. Materials, Inc., the company contracted to handle the materials. During this transfer, extreme care was taken to avoid direct contact and consequent contamination of the bottle surface. The bottles were held by their plastic-wrapped lids and the bottom plastic bag was pulled away from the body of the bottle. The bottle was then placed into the gloved hand of the person receiving on the other side of the fence who then pulled away the plastic bag from over the lid. The plastic coverings were disposed of in containers on the contaminated side of the fence. The bottles were taken to a service truck for repackaging for shipment to the contract laboratory.

#### 4.2.1 Sample Labels

EPA Sample Control Center (SCC) labeling procedures were followed during the study in order to prevent misidentification of samples. The labels were completed and affixed to the sample containers prior to sampling. The sampling ID numbers, supplied by the Sample Analysis Center, were affixed to the individual bottles and individual cases.

#### 4.2.2 Sample Preservation

Once a sample was collected, steps were taken to preserve the chemical and physical integrity of the sample during transport and storage prior to analysis. Soil samples were kept away from light to avoid any further photo-oxidation. However, no effort was made to quench the chemical reactions produced by the APEG.

#### 4.2.3 Sample Shipment

The samples were shipped as Class B Poisons in accordance with DOT-E-7909 specifications. All samples were shipped using an appropriate commercial overnight delivery service (e.g., Federal Express). All sampling personnel familiarized themselves with the delivery service requirements for shipment of Class B Poisons and environmental samples.

The samples were transported to a contract laboratory as soon as possible and not exceeding 3 days from the time the first sample was collected. Prior to shipment, all sample lids were tightened and the glass bottles were individually wrapped in plastic bags, individually packed in metal paint cans, and

cushioned by an absorbent material, e.g., vermiculite, to prevent contact with other objects and to eliminate breakage. All paint cans were sealed with clips and labeled as follows:

- Poison
- Danger
- Poison B, solid, N.O.S.
- Sample.

The paint cans were then placed inside a DOE 12B cardboard box for shipping. The outside of the DOT 12B box contained specific identification on the labels and certain information for environmental samples as follows:

- Poison
- Danger
- Poison B, solid, N.O.S.
- Number of samples in shipment
- Batch number of shipment.

The SCC was notified immediately upon arrival of the shipment and their personnel were prepared to receive the samples. Immediately after the shipment arrived, the designated laboratory was contacted and the following information relayed:

- Sample numbers
- Name of carrier (method of transport)
- Airbill numbers
- Date and time of shipment
- Estimated data and time of delivery
- Any problems relating to shipment.

4.2.4 Sample Custody

Because litigation was not involved in this project, no chain-of-custody was used other than the service provided by Federal Express. A manifest form was included with the Dioxin Traffic report (see Figure 4) in order to comply with the regulations regarding the shipment of hazardous material. Each sample container was identified with the appropriate preprinted label provided with each sample delivery's traffic report. The first page of each Dioxin Traffic Report was then sent to the SCC. The second page was sent to the

Page

Date of Shipment _____

*Please sign and date all copies. You may retain one copy for your records; return the remaining copies in the envelope provided to:

James B. White
Office for Hazardous Materials Research
Research Triangle Institute
P. O. Box 12194
Research Triangle Park, NC 27709-9981

This is to acknowledge that on behalf of:

James B. White
Office for Hazardous Materials Research
Research Triangle Institute
P. O. Box 12194
Research Triangle Park, NC 27709-9981

Radioactive Materials License Number:

DEA Registration Number:

DEA Order Form Number:

Permit to Export Number:

I have received the following materials:

_____ soil samples contaminated with dioxin (Case Number 2913)

*Date:_____

_____
Signature of Authorized Signature

Figure 4. Shipment manifest form.

Sample Management Office. The third page was retained as part of the sampling worker's record of delivery. The remaining pages of the Dioxin Traffic Report were inserted into the boxes and shipped with the sample containers to the laboratories indicated on the traffic report: (page 4 to Duluth ERL; page 5 to Bay, St. Louis; and page 6 to the designated contractor laboratory).

4.2.5 Personnel and Site Safety

The necessary protective clothing was provided by O.H. Materials, Inc. Due to the nature of the hazard, i.e., 2,3,7,8-TCDD, EPA Level C protective clothing and equipment were required to ensure personnel safety. Level C protection includes pesticide-resistant gloves, full pesticide-resistant, disposable coveralls, e.g., Saran-coated, and a full-face respirator with a pesticide and organic vapor cartridge.

In addition to protective clothing, O.H. Materials was responsible for site safety. In addition to standard protective hygiene measures, a 20- by 20-foot area located next to the site was provided as a decontamination area. Individuals within the site removed all of their disposable clothing before leaving the area. These items were placed in large plastic bags located within the area that were then placed inside the stable when the field work was completed.

In an effort to reduce the volume of contaminated trash and rinse water, workers made a conscious effort to minimize the amount of equipment and supplies brought onto the site. Only disposable protective clothing were used. All footwear, once worn inside the site, remained on site until completion of the field work. In addition, all equipment including Rototillers, cameras, and shovels were boxed and stored on site. At the end of each day, disposable clothing was removed and disposed of in plastic bags. Individuals were expected to shower thoroughly as soon as possible after leaving the job site.

4.3 CLEAN-UP TECHNIQUES

Sample collection was done using a combination of acetate and stainless steel coring tubes. The acetate tubes were used only on the untreated plots. They were used only once for a single composite sample, i.e., 16-point samples. They were then discarded in order to prevent the cross-contamination of plots via contaminated tubes. The stainless steel tubes were used only on the

APEG-treated and the MPEG-treated plots and only once to composite a single sample, i.e., 16-point samples; they were not discarded afterward. Instead, they were collected and cleaned immediately prior to use on the following sample visit. The clean-up procedure involved the following steps:

1. At the completion of a site visit, the stainless tubes were placed in a container of water and left to soak until the return trip.

2. Upon the workers' return, the tubes were rinsed off and soaked in fresh water for 1/2 hour.

3. A paper towel was then pushed through the barrel of each tube to remove all water and any residue.

4. The tubes were rinsed again with water and dried with paper towel.

5. The tubes were then rinsed with hexane using a squeeze-bottle; then with an acetone rinse, also from a squeeze-bottle.

6. The tubes were then stacked on a dust-free surface and covered with paper towels until needed.

# SECTION 5

# TREATMENT

Treatment involved the application of APEG/MPEG to a designated plot followed by the covering of appropriate plots. The APEG reagent was prepared per Franklin Research Center specifications by Callery Chemical Company, Callery, Pennsylvania, using Carbowax methoxy 350 as a starting material. The actual formulation was considered to be proprietary and was not made known to RTI. In addition to the APEG, a 55-gallon barrel of Carbowax methoxy 350 was purchased from Union Carbide, Charleston, West Virginia, to be used as a control. Both the APEG and MPEG were delivered to the site by O.H. Materials, Inc.

## 5.1 INITIAL TREATMENT

The plots designated A and C were given a single treatment of APEG. The initial treatment consisted of filling a 2-gallon steel watering can having a perforated spray cap with 7 liters of APEG. The reagent was then dispersed over the surface of a plot and allowed to fill the frame. The surface of the treated plots was then raked and stirred to a depth of approximately 3 inches with a three-pronged garden tool in order to mix the APEG with the soil. Those plots designated as E received a similar treatment using 7 liters of MPEG. Those plots designated as B and D were left untreated. Their surfaces, however, were raked to simulate the mixing that has occurred in A, C, and E.

The plots designated by the letters A and B were covered with 0.5 mm black polyethylene plastic. A 3½-foot, 1-inch by 1-inch dowel was centered horizontally over the sampling frame to provide central elevation for the covering and to promote the drainage of condensate to the sides of the plot. The 5-foot by 5-foot plastic squares were then placed over the frame.

## 5.2 ADDITIONAL TREATMENTS

Additional treatments involved the application of a 2 to 1 toluene-APEG mixture to those sites previously treated with APEG alone. The MPEG treatments were not modified. The covers from the treated sites were carefully removed

to prevent cross-contamination with soil and to prevent any moisture collected on the interior of the covering from falling into the plot area. A second series of samples were collected in the manner prescribed in Section 4, Sampling Protocol. A second treatment was applied in the manner prescribed in Section 5.1, Treatment. The designated sites were again recovered. This procedure was repeated on two separate site visits. There were a total of three treatments, including the initial treatment.

The previously identified bleacher was also treated during the third visit. A standard 3-gallon hand-pressurized agricultural sprayer was used. The sprayer was filled with a 2 to 1 toluene-APEG mixture and the spray nozzle was tested to see that it would emit a uniform spray.

After adjusting the spray nozzle, the sprayer was refilled and two designated 31-foot by 9.6-foot (302.4 square feet) sections of the bleacher were each sprayed with approximately 1½ gallons of reagent. An attempt was made to maintain an even distribution over the area. However, the spray nozzle malfunctioned due to accumulated APEG and uneven distribution of the mixture resulted.

## SECTION 6

## ANALYTICAL PROCEDURES

The analytical procedures used in this project included both chemical and statistical methods. The chemical analyses were performed at a series of contract laboratories designated by the Sample Management Office. The statistical analyses were performed in-house at RTI.

### 6.1 SAMPLE ANALYSIS PROCEDURES

The analysis of the samples for 2,3,7,8-TCDD was performed under the auspice of the Superfund National Dioxin Study. Consequently, a series of four contract laboratories were assigned by the Sample Management Office, Alexandria, Virginia. They were as follows:

- Envirodyne
  12161 Lackland
  St. Louis, MO 63141

- Geochem
  16910 Parkrow
  Houston, TX 77084

- ETC
  284 Raratan Center Parkway
  Edison, NJ 08837

- Meade Compuchem
  3308 Chapel Hill/Nelson Hwy.
  Research Triangle Park, NC 27709

All analyses were performed in accordance with the contract obligations required of these laboratories under the study. A copy of the analytical requirements are contained in Appendix B. The results of the analyses specifically related to the arena site are contained in Tables 2 through 6. The tables are arranged to show the sampling data from a single category of plots that received the same treatment. The data are also arranged so as to cover the time period of four site visits. The results of the overall sampling effort including the

TABLE 2. ANALYTICAL RESULTS: A PLOTS (APEG, COVERED)

| Trip number | Column 1 - Row 4 | | Colume 2 - Row 2 | | Column 3 - Row 3 | | Column 4 - Row 1 | | Column 5 - Row 5 | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Sample No. | (ppb) | Sample No. | (ppb) | Sample No. | (ppb) | Sample No. | (ppb) | Sample No. | (ppb) |
| 1 | DX000116 | 92.2 | DX000107 | 91.5 | DX000113 | 97.9 | DX000104 | 96.9 | DX000207 | 58.8 |
| | DX000317 | 117 | DX000214 | 83.9 | DX000302 | ---- | DX000211 | 90.1 | DX000314 | ---- |
| 2 | DX000416 | 56 | DX000407 | 124 | DX000413 | 114 | DX000404 | 109 | DX000506 | 125 |
| | DX000602 | 85 | DX000513 | 110 | DX000519 | 139 | DX000510 | 124 | DX000611 | --- |
| 3 | DX000716 | 86 | DX000707 | 86 | DX000713 | 84 | DX000704 | 86 | DX000808 | --- |
| | DX000907 | 104 | DX000815 | -- | DX000904 | 91 | DX000812 | -- | DX000916 | 64.1 |
| 4 | DX001016 | 58 | DX001007 | 64 | DX001013 | 59 | DX001004 | 65 | DX001106 | 91 |
| | DX001203 | 121 | DX001113 | 69 | DX001117 | 78 | DX001110 | 62 | DX001212 | --- |

"-" indicates data not received.

TABLE 3. ANALYTICAL RESULTS: B PLOTS (NOT TREATED, COVERED)

| Trip | Column 1 - Row 3 | | Column 2 - Row 5 | | Column 3 - Row 1 | | Column 4 - Row 4 | | Column 5 - Row 2 | |
|---|---|---|---|---|---|---|---|---|---|---|
| number | Sample No. | (ppb) | Sample No. | (ppb) | Sample No. | (ppb) | Sample No. | (ppb) | Sample No. | (ppb) |
| 1 | DX000111 | 103 | DX000204 | 89.2 | DX000163 | 96.5 | DX000201 | 89.2 | DX000110 | 99.7 |
| | DX000218 | 98.9 | DX000311 | 92.9 | DX000210 | 82.6 | DX000308 | 115 | DX000217 | 94.5 |
| 2 | DX000411 | 96 | DX000503 | 112 | DX000403 | 99 | DX000419 | 166 | DX000410 | 102 |
| | DX000517 | 121 | DX000608 | 78 | DX000509 | 103 | DX000605 | 127 | DX000516 | 130 |
| 3 | DX000711 | 103 | DX000805 | -- | DX000703 | 94 | DX000802 | -- | DX000710 | 108 |
| | DX000902 | 113 | DX000913 | 14.6 | DX000811 | -- | DX000910 | 129 | DX000901 | 128 |
| 4 | DX0001011 | 114 | DX001103 | 149 | DX001003 | 109 | DX001019 | 103 | DX001010 | 127 |
| | DX001117 | 130 | DX001209 | 144 | DX001110 | 140 | DX001206 | 143 | DX001116 | 114 |

TABLE 4. ANALYTICAL RESULTS: C PLOTS (APEG, UNCOVERED)

| Trip | Column 1 - Row 3 | | Column 2 - Row 5 | | Column 3 - Row 1 | | Column 4 - Row 4 | | Column 5 - Row 2 | |
|---|---|---|---|---|---|---|---|---|---|---|
| Number | Sample No. | (ppb) | Sample No. | (ppb) | Sample No. | (ppb) | Sample No. | (ppb) | Sample No. | (ppb) |
| 1 | DX000105 | 103 | DX000117 | 93.9 | DX000205 | 86.7 | DX000114 | 101 | DX000105 | 103 |
| | DX000212 | 89.3 | DX000306 | 116 | DX000312 | -- | DX000303 | -- | DX000212 | 89.3 |
| 2 | DX000405 | 100 | DX000417 | 145 | DX000504 | 84. | DX000414 | -- | DX000405 | 100 |
| | DX000511 | 87 | DX000603 | 96 | DX000609 | 88 | DX000520 | 130 | DX000511 | 87 |
| 3 | DX000705 | 72 | DX000717 | 77 | DX000805 | -- | DX000714 | 74 | DX000705 | 72 |
| | DX000813 | -- | DX000908 | 82 | DX000914 | 73.3 | DX000905 | N.D. | DX000813 | -- |
| 4 | DX001005 | 93 | DX001017 | 56 | DX001104 | 94 | DX001014 | 68 | DX001005 | 93 |
| | DX001111 | 91 | DX001204 | 65 | DX001210 | 86 | DX001201 | 95 | DX001111 | 91 |

"--" indicates not received.
N.D. not detected.

TABLE 5. ANALYTICAL RESULTS: D PLOTS (NOT TREATED, UNCOVERED)

| Trip number | Column 1 - Row 1 | | Column 2 - Row 3 | | Column 3 - Row 2 | | Column 4 - Row 5 | | Column 5 - Row 4 | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Sample No. | (ppb) | Sample No. | (ppb) | Sample No. | (ppb) | Sample No. | (ppb) | Sample No. | (ppb) |
| 1 | DX000101 | 91.9 | DX000112 | 77.9 | DX000108 | 104 | DX000206 | 91.8 | DX000202 | 93.8 |
| | DX000208 | 84.6 | DX000301 | ---- | DX000215 | 89.6 | DX000313 | ---- | DX000309 | 120 |
| 2 | DX000401 | 64 | DX000412 | ---- | DX000408 | 153 | DX000505 | 97 | DX000501 | 57 |
| | DX000507 | 113 | DX000518 | 145 | DX000514 | 112 | DX000610 | 112 | DX000606 | 155 |
| 3 | DX000701 | 96 | DX000712 | 115 | DX000708 | 106 | DX000807 | ---- | DX000803 | --- |
| | DX000309 | -- | DX000903 | 119 | DX000816 | -- | DX000915 | 143 | DX000911 | 144 |
| 4 | DX001001 | 94 | DX001012 | 117 | DX001008 | 112 | DX001105 | 145 | DX001101 | 161 |
| | DX001107 | 148 | DX001118 | 163 | DX001114 | -- | DX001211 | 148 | DX001207 | 186 |

TABLE 6. ANALYTICAL RESULTS: E PLOTS (MPEG, UNCOVERED)

| Trip number | Column 1 - Row 5 | | Column 2 - Row 1 | | Column 3 - Row 4 | | Column 4 - Row 2 | | Column 5 - Row 3 | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Sample No. | (ppb) | Sample No. | (ppb) | Sample No. | (ppb) | Sample No. | (ppb) | Sample No. | (ppb) |
| 1 | DX000102 | 110 | DX000203 | 89.6 | DX000118 | 92.8 | DX000109 | 104 | DX000115 | 97.1 |
| | DX000209 | 90.9 | DX000310 | 108 | DX000307 | 91.4 | DX000216 | 90.1 | DX000304 | --- |
| 2 | DX000402 | 73 | DX000502 | 88 | DX000418 | 88 | DX000409 | 121 | DX000415 | 127 |
| | DX000508 | 105 | DX000607 | 107 | DX000604 | 98 | DX000515 | 91 | DX000601 | 106 |
| 3 | DX000702 | 82 | DX000804 | -- | DX000801 | -- | DX000709 | 61 | DX000715 | 92 |
| | DX000810 | -- | DX000912 | 101 | DX000909 | 105 | DX000817 | -- | DX000906 | 153 |
| 4 | DX001002 | 88 | DX001102 | 81 | DX001018 | 82 | DX001009 | 86 | DX001015 | 97 |
| | DX001108 | 110 | DX001208 | 64 | DX001205 | 95 | DX001115 | 95 | DX001202 | 94 |

"--" indicates not received.

bleacher sites and other points outside the stable arena are contained in Appendix C.

## 6.2 STATISTICAL ANALYSIS PROCEDURES

The basic experimental design for the Shenandoah Stable site consisted of a 5 by 5 Latin square involving 25 plots (identified by row and column). The five treatments, designated by the letters A through E, as shown below, were randomly assigned within the Latin square configuration:

- A = APEG treated, covered
- B = Not treated, covered
- C = APEG treated, uncovered
- D = Not treated, uncovered
- E = MPEG treated, uncovered

Duplicate measurements of dioxin concentration levels within each of the plots were made four times: the first pair of measurements during a baseline period (prior to application of any treatment) and the remaining pairs after each of the three treatment applications.

The statistical analyses were conducted in accordance with the above-described experimental design, although some compensation for missing observations were made; some of the analyses were based on plot-specific means (i.e., a mean of the duplicate observations where available, and the single observation within the plot when one observation was missing). Three basic types of statistical analyses were conducted, as described in the following subsections. All of these analyses were performed using the SAS[1/] statistical analysis software package--in particular, the MEANS and GLM procedures. All analyses were performed using the Triangle Universities Computation Center (TUCC).

### 6.2.1 Generation of Descriptive Statistics

The purpose of these analyses is to furnish simple tabular and graphical summaries of the data. The results are given by treatment and/or time and include sample sizes, means, and standard errors of the means. Also, the standard deviation of the duplicate measurements within plots (pooled over plots) is included among the descriptive results. This provides a measure of the sampling/measurement variability.

### 6.2.2 Analysis of Variance of Dioxin Concentrations at Each Measurement Time

At each measurement time (excluding baseline) the effects of the treatments on dioxin levels are assessed through an analysis of variance (ANOVA) approach. The purpose is to determine if dioxin levels for the different treatments at a given time are different. The underlying model for the analysis, which is based on the Latin square design, is given by

$$Y_{ij(k)\ell} = \mu + \alpha_i \quad \beta_j + \tau_{(k)} + \varepsilon_{ij} + \delta_{ij\ell} \qquad (1)$$

where

$Y_{ij(k)\ell}$ = the $\ell^{th}$ observed dioxin level ($\ell$ = 1,2) for row i, column j, and treatment k (the subscript k is enclosed in parentheses since k is a function of i and j)

$\mu$ = the overall mean dioxin level (at a given time)

$\alpha_i$ = effect of the $i^{th}$ row on dioxin level

$\beta_j$ = effect of the $j^{th}$ column on dioxin level

$\tau_{(k)}$ = effect of the $k^{th}$ treatment on dioxin level

$\varepsilon_{ij}$ = random error effect associated with plot (i,j)

$\delta_{ij\ell}$ = random measurement/sampling error for observation $\ell$ in plot (i,j).

Both the plot error and measurement error components are assumed to be normally distributed with zero means and constant variances. In order to estimate the model parameters, it is necessary to assume also that there are no interaction effects among the rows, columns, and treatments (a consequence of the Latin square design). Some insight into the validity of this zero interaction assumption is provided by conducting an analysis of variance of the baseline data, since row by column interactions, for instance, can be estimated for that time period.

The analysis of variance procedure partitions the total variation in the n dioxin measurements (at a given time) into row, column, and treatment components, as shown here.

| Source of variation | Degree of freedom | Mean squares |
|---|---|---|
| Among plots | 24 | |
| Rows | 4 | $MS_R$ |
| Columns | 4 | $MS_C$ |
| Treatments | 4 | $MS_T$ |
| Remainder | 12 | $MS_e$ |
| Within plots | n-25 | $MS_\delta$ |

The "remainder" component corresponds to the plot error component in the model, while the "within plots" component is the measurement error component. An overall test for treatment differences is provided by the F statistic,

$$F = MS_T/MS_e \qquad (2)$$

which is compared to the tabulated F distribution with 4 and 12 degrees of freedom.

6.2.3 Analysis of Variance of Changes in Dioxin Concentrations Over Time

These analyses are directed at determining if treatments affect changes in dioxin levels over time. The means within each plot at each given time are first computed. Then differences between the corresponding plot means at two different times are calculated. Let $Z_{ij(k)}$ denote such difference for the $i^{th}$ row and $j^{th}$ column. In particular, let $Z^{(1)}_{ij(k)}$, $Z^{(2)}_{ij(k)}$, and $Z^{(3)}_{ij(k)}$ denote, respectively, the differences for (Time 2 minus Time 1), (Time 3 minus Time 1), and (Time 4 minus Time 1), where Time 1 is the baseline period. Such differences are then analyzed according to the usual Latin square model

$$Z^{(t)}_{ij(k)} = \mu^{(t)} + \alpha^{(t)}_i + \beta^{(t)}_j + \gamma^{(t)}_{(k)} + \varepsilon^{(t)}_{ij}, \quad t = 1,2,3 \qquad (3)$$

where the parameters and assumptions are analogous to those defined for the previous model. Similar models, of course, would apply to differences between the dioxin levels at any other pair of times; e.g., Time 4 minus Time 2. Overall tests for treatment effects were performed using an F test (based on 4 and 12 degrees of freedom) like that in Equation (2).

In conjunction with the ANOVA of dioxin-level changes over time, pair-wise comparisons of the various treatments were performed. These comparisons were made using Tukey's multiple comparison procedure, with a significance level of 0.05 (see Steel and Torrie 1980, for instance).

## SECTION 7

## STATISTICAL ANALYSIS RESULTS

### 7.1 STATISTICAL ANALYSIS

The measured dioxin concentrations used in the statistical analyses described in this section are given in Tables 2 through Table 6. Plot-specific means, by time of measurement, are provided in Table 7. Time 1 designates the baseline period, prior to treatment of the plots, while Times 2, 3, and 4 represent the measurements taken following the sequential application of the indicated treatments.

The concentration data are further summarized in Table 8. Part (a) of this table provides the means of the concentrations, by treatment and time, when equal weights are attached to plots (i.e., simple averages of the five-plot-specific means shown in Table 7). Part (b) of this table shows the corresponding means when equal weights are associated with the individual observed concentrations (i.e., simple means of the values shown in Appendix C). In the absence of missing data, the means in Parts (a) and (b) of Table 8 would coincide. Part (c) of Table 8 shows the number of individual concentration measurements upon which the means of Part (b) are based, and Part (d) shows the associated standard errors of these estimated mean dioxin concentrations. Because of the imbalance in the number of observations among rows, columns, and treatments created by the missing observations, differences between the means shown in Part (b) of the table may not accurately reflect the treatment effects if dioxin levels vary substantially over rows and/or columns. The general agreement between the corresponding means shown in Parts (a) and (b), however, suggest that such extreme row and/or column effects are not present.

A plot of the mean dioxin concentrations over time is given in Figure 5.

As indicated in Section 6.2, an analysis of variance was performed on the data of Appendix C for each measurement time. Results of these analyses are presented in Table 9. No evidence of row or column effects was found for

TABLE 7. PLOT-SPECIFIC MEANS OF DIOXIN CONCENTRATIONS (ppb), BY MEANS OF MEASUREMENT[1/]

| Definition of plot[2/] | | | Measurement time[3/] | | | |
|---|---|---|---|---|---|---|
| Treatment | Row | Column | Time 1 | Time 2 | Time 3 | Time 4 |
| A | 1 | 4 | 93.50 | 116.50 | 86.00 | 63.50 |
| | 2 | 2 | 87.70 | 117.00 | 86.00 | 66.50 |
| | 3 | 3 | 97.90 | 126.50 | 87.50 | 68.50 |
| | 4 | 1 | 104.60 | 96.00 | 95.00 | 89.50 |
| | 5 | 5 | 58.80 | 125.00 | 69.10 | 91.00 |
| B | 1 | 3 | 89.55 | 101.00 | 94.00 | 124.50 |
| | 2 | 5 | 97.10 | 116.00 | 118.00 | 120.50 |
| | 3 | 1 | 100.95 | 108.50 | 108.00 | 122.00 |
| | 4 | 4 | 102.10 | 146.50 | 129.00 | 123.00 |
| | 5 | 2 | 91.05 | 95.00 | 14.60 | 149.00 |
| C | 1 | 5 | 96.15 | 93.50 | 72.00 | 92.00 |
| | 2 | 1 | 71.45 | 74.00 | 74.00 | 74.00 |
| | 3 | 4 | 101.00 | 130.00 | 74.00 | 81.00 |
| | 4 | 2 | 104.95 | 120.50 | 79.50 | 60.50 |
| | 5 | 3 | 86.70 | 86.00 | 73.30 | 90.00 |
| D | 1 | 1 | 88.25 | 104.00 | 96.00 | 146.00 |
| | 2 | 3 | 96.80 | 132.50 | 106.00 | 112.00 |
| | 3 | 2 | 77.90 | 145.00 | 117.00 | 140.00 |
| | 4 | 5 | 106.90 | 106.00 | 144.00 | 173.50 |
| | 5 | 4 | 91.80 | 104.50 | 143.00 | 146.50 |
| E | 1 | 2 | 100.45 | 110.50 | 82.00 | 99.00 |
| | 2 | 4 | 97.05 | 106.00 | 61.00 | 90.50 |
| | 3 | 5 | 97.10 | 116.50 | 122.50 | 95.50 |
| | 4 | 3 | 92.10 | 93.00 | 105.00 | 88.50 |
| | 5 | 1 | 98.80 | 97.50 | 101.00 | 72.50 |

1/ Underlined values are single observed concentrations; other values represent the means of the two observations within a plot.

2/ See Section 5.2 for treatment definitions.

3/ Time 1 is the baseline period, prior to application of treatments.

TABLE 8. SUMMARY OF DIOXIN CONCENTRATIONS, BY TREATMENT AND TIME OF MEASUREMENT

| | Treatment | Time of measurement | | | |
|---|---|---|---|---|---|
| | | Time 1 | Time 2 | Time 3 | Time 4 |
| • Average of plot-specific dioxin concentrations (ppb)[1/] | A | 88.5 | 116.2 | 84.7 | 75.8 |
| | B | 96.2 | 113.4 | 92.7 | 127.8 |
| | C | 92.1 | 100.8 | 74.6 | 79.6 |
| | D | 92.3 | 118.4 | 121.2 | 143.6 |
| | E | 97.1 | 104.7 | 94.3 | 89.2 |
| • Average of individual dioxin concentration measurements (ppb)[2/] | A | 91.0 | 115.2 | 86.6 | 74.1 |
| | B | 96.2 | 113.4 | 98.5 | 127.8 |
| | C | 91.6 | 100.5 | 75.4 | 79.6 |
| | D | 94.2 | 115.4 | 120.5 | 147.1 |
| | E | 97.1 | 104.7 | 99.0 | 89.2 |
| • Number of observations upon which means of Part (b) are based | A | 8 | 9 | 7 | 9 |
| | B | 10 | 10 | 7 | 10 |
| | C | 8 | 8 | 6 | 10 |
| | D | 8 | 9 | 6 | 9 |
| | E | 9 | 10 | 6 | 10 |
| • Standard errors of the means shown in Part (b) (ppb)[2/] | A | 5.7 | 5.1 | 3.9 | 6.8 |
| | B | 2.8 | 7.7 | 14.8 | 5.4 |
| | C | 5.9 | 8.6 | 1.5 | 4.4 |
| | D | 4.5 | 10.6 | 8.0 | 11.5 |
| | E | 2.7 | 4.3 | 12.6 | 3.4 |

1/ Means shown in Table 2 are treated equally, even though some are based on single observations and others are based on duplicate observations.

2/ Row and column effects are ignored; their effects, if present, may cause biases in the reported estimates of means and standard errors, since imbalance in the Latin square design is created when missing observations occur.

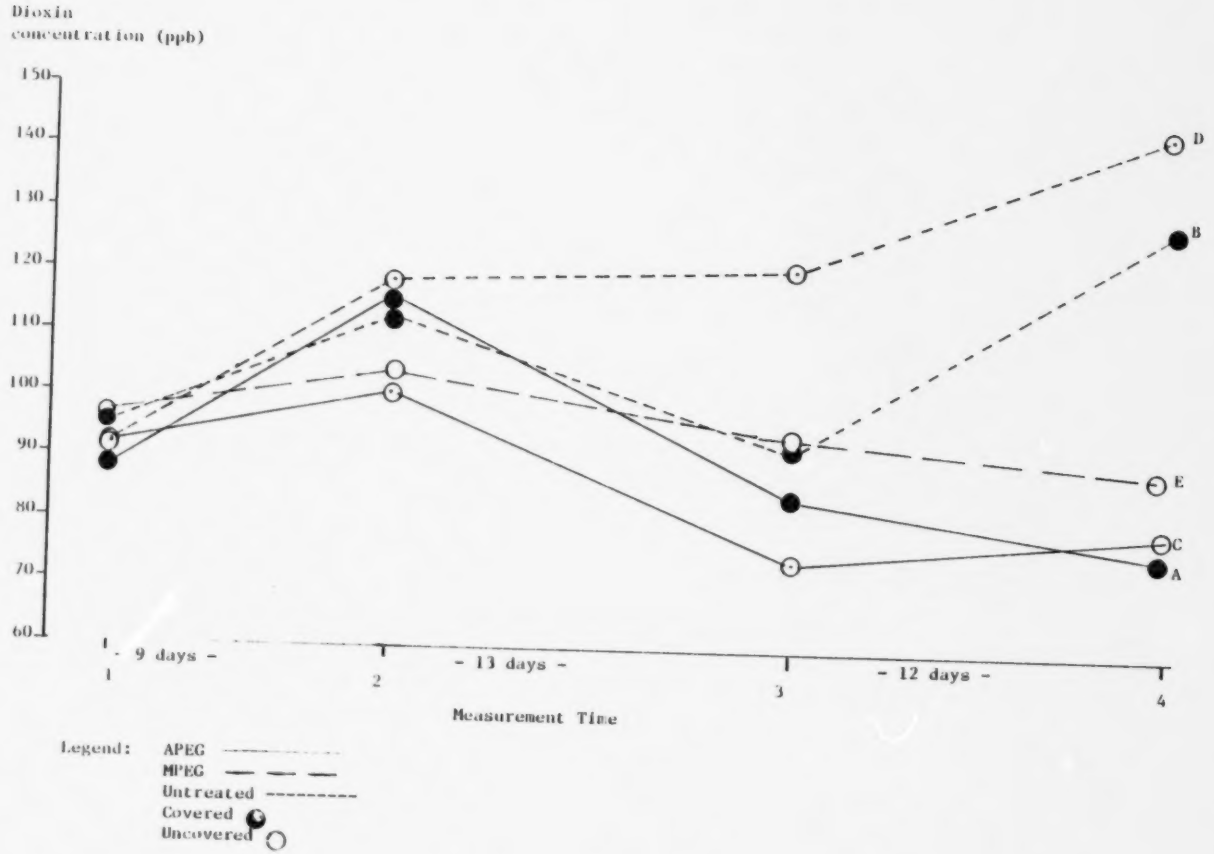



Figure 5. Estimated mean dioxin concentrations versus measurement time.

TABLE 9. RESULTS FROM ANALYSIS OF VARIANCE ON DIOXIN CONCENTRATIONS AT FOUR MEASUREMENT TIMES

| Variable | Source of variation | Degrees of freedom | Sums of squares[1/] | Mean squares | F statistic[3/] |
|---|---|---|---|---|---|
| D1=dioxin concentration (ppb) at time 1 (baseline) | Among plots | 24 | 4073.1 | 169.7 | |
| | rows | 4 | 1138.2 | 284.6 | 1.33 |
| | columns | 4 | 112.1 | 28.0 | 0.13 |
| | treatments | 4 | 321.1 | 80.7 | 0.38 |
| | remainder | 12 | 2566.5 | 213.9 | |
| | Within plots | 18 | 2345.4 | 130.3 | |
| | Total | 42 | 6418.5 | | |
| D2=dioxin concentration (ppb) at time 2 | Among plots | 24 | 11719.4 | 488.3 | |
| | rows | 4 | 2837.5 | 709.4 | 1.75 |
| | columns | 4 | 2768.8 | 692.2 | 1.71 |
| | treatments | 4 | 1545.9 | 386.5 | 0.95 |
| | remainder | 12 | 4858.1 | 404.8 | |
| | Within plots | 21 | 10987.5 | 523.2 | |
| | Total | 45 | 22706.9 | | |
| D3=dioxin concentration (ppb) at time 3 | Among plots | 24 | 21073.8 | 878.1 | |
| | rows | 4 | 3731.2 | 932.8 | 1.45 |
| | columns | 4 | 3269.2 | 817.3 | 1.27 |
| | treatments | 4 | 7326.8 | 1831.7 | 2.85 |
| | remainder | 12 | 7701.8 | 641.8 | |
| | Within plots | 7 | 2317.5 | 331.1 | |
| | Total | 31 | 23391.3 | | |
| D4=dioxin concentration (ppb) at time 4 | Among plots | 24 | 45740.5 | 1905.9 | |
| | rows | 4 | 1243.7 | 310.9 | 0.79 |
| | columns | 4 | 1454.5 | 363.6 | 0.93 |
| | treatments | 4 | 35739.4 | 8934.8 | 22.74* |
| | remainder | 12 | 4714.0 | 392.8 | |
| | Within plots | 23 | 11413.0 | 496.2 | |
| | Total | 47 | 57153.5 | | |

1/ The reported sums of squares for rows, columns, and treatments are adjusted for the other effects (e.g., rows are adjusted for columns and treatments). Hence the sums of squares for rows, columns, treatments, and remainder do not add to the overall "among-plots" sum of squares.

2/ Based on Equation (2).

* F value is statistically significant at 0.01 level.

any of the four time periods. A highly significant treatment effect was found for the fourth time period; treatment effects for the remaining times were not statistically significant, although the Time 3 treatment effect was marginal (statistically significant at a 0.10 level of significance). The nonsignificant treatment result for the baseline period suggests that the plots selected to receive the treatment (subsequently) were not initially different in terms of their dioxin concentration levels.

An alternative partition of the overall sum of squares appropriate for the baseline period involves pooling the treatments and remainder components. This combined component, yielding a mean square of 180.5 with 16 degrees of freedom, contains both plot error and row-by-column interaction effects, in addition to measurement-error. Comparison of this mean square with the within-plots mean square (equal to 130.3) via an F test produces an F value of 1.39, which is not statistically significant. This result suggests that row-by-column interaction effects were not present, at least for the baseline period. This also tends to support the assumption of "no interaction" that is necessary for the Latin square design to yield unbiased estimates of treatment effects.

The within-plot mean squares shown in Table 9 represent the pooled variances of the duplicate concentration measurements made within (some of) the plots. Square roots of these mean squares therefore provide estimated standard deviations for characterizing the sampling/measurement error of the dioxin concentrations

| Measurement time | Estimated sampling/ measurement error variance | Estimated sampling/ measurement standard deviation (ppb) |
|---|---|---|
| 1 | 130.3 | 11.4 |
| 2 | 523.2 | 22.9 |
| 3 | 331.1 | 18.2 |
| 4 | 496.2 | 22.3 |

Pooling of these variances across the four measurement times yields a measurement error variance of 392.2 (with 69 degrees of freedom) or a standard deviation of 19.8 ppb.

Analysis of variance of the dioxin concentrations shown in Table 7 for each of the measurement times was also performed; in addition, to assess the effects of the treatments on changes in dioxin levels over time, differences

between the concentrations at two different times were calculated and an analysis of variance on these differences was performed. The analyses are based on the Equation (3), and the results of the analyses are given in Table 10. In this table, the D1, D2, D3, and D4 variables represent the dioxin concentrations as given in Table 7, and the differences D2-D1, D3-D1, etc. represent the differences between the concentrations at Times 2 and 1, at Times 3 and 1, etc. Significant row and column effects were not detected for any of the variables listed in Table 10. The last column of the table indicates those cases for which nonsignificant and significant treatment effects were detected via the F test. Statistically significant treatment effects were found for D4 (in agreement with the previously described analyses) and for the differences D4-D1 and D4-D2. For these three cases, the results of Tukey's pair-wise comparison procedure (using significance level equal to 0.05) are indicated by the underscoring of those treatment means that are not statistically different. For the Time 4 minus Time 1 variate, for example, this procedure indicates that the A, C, and E means are not statistically different; that the E and B means are not statistically different; and that the B and D means are not statistically different. Table 11 provides the differences between the treatment pairs for the D4-D1 and D4-D2 variates and again designates the results of Tukey's pair-wise comparison procedure (0.05 significance level).

The results of these tables are fairly clear:

1. The two APEG treatments (Treatments A and C) appear to be effective in reducing dioxin levels, or in reducing the apparent increase in dioxin levels, when compared to the untreated cases. However, this does not appear to happen prior to the fourth measurement time. Estimated <u>percent</u> changes in dioxin levels between Times 1 and 4 are shown below:

| Treatment | Time 4 minus baseline estimated change percent |
|---|---|
| A = APEG, covered | -19 |
| B = APEG, uncovered | -15 |
| C = MPEG, uncovered | - 4 |
| D = Untreated, covered | +37 |
| E = Untreated, uncovered | +54 |

2. The APEG treatments cannot be declared statistically different from the MPEG (uncovered) treatment, though their <u>estimated</u> reductions in dioxin levels tend to be larger.

3. Little or no benefit appears to be derived by covering the APEG-treated plots.

TABLE 10. MEAN DIOXIN LEVELS AND MEAN CHANGES OVER TIME IN DIOXIN LEVELS, IN ppb, BY TREATMENT

| Variable | Treatments | | | | | Significance of treatment effect[1/] |
|---|---|---|---|---|---|---|
| | A | C | E | B | D | |
| | APEG, covered | APEG, uncovered | MPEG, uncovered | Untreated covered | Untreated, uncovered | |
| D1 | 88.5 | 92.1 | 97.1 | 96.2 | 92.3 | NS |
| D2 | 116.2 | 100.8 | 104.7 | 113.4 | 118.4 | NS |
| D3 | 84.7 | 74.6 | 94.3 | 92.7 | 121.2 | NS |
| D4 | 75.8 | 79.6 | 89.2 | 127.8 | 143.6 | |
| D2-D1 | 27.7 | 8.8 | 7.6 | 17.3 | 26.1 | NS |
| D3-D1 | -3.8 | -17.5 | -2.8 | -3.4 | 28.9 | NS |
| D4-D1 | -12.7 | -12.5 | -7.9 | 31.7 | 51.3 | ** |
| D3-D2 | -31.5 | -26.2 | -10.4 | -20.7 | 2.8 | NS |
| D4-D2 | -40.4 | -21.2 | -15.5 | 14.4 | 25.2 | * |
| D4-D3 | -8.9 | 5.0 | -5.1 | 35.1 | 22.4 | NS |

1/ NS = not statistically significant at 0.05 level.
* = statistically significant at 0.05 level.
** = statistically significant at 0.01 level.

2/ In cases where statistically significant is indicated, those means which are not statistically different from one another are underscored. The criterion is based on Tukey's multiple comparison procedure, using an overall significance level of 0.05.

TABLE 11. SUMMARY OF PAIRWISE TREATMENT COMPARISONS FOR CHANGES IN DIOXIN LEVELS BETWEEN TIMES 1 AND 4 AND BETWEEN TIMES 2 AND 4

| Treatment difference | Description of comparison | Mean treatment difference (ppb) D4 - D1 | D4 - D1 |
|---|---|---|---|
| A-D | [APEG, covered] vs. [not treated, uncovered] | -64.0* | -65.6* |
| A-B | [APEG, covered] vs. [not treated, covered] | -44.4* | -54.8* |
| A-E | [APEG, covered] vs. [MPEG, uncovered] | -4.8 | -24.9 |
| A-C | [APEG, covered] vs. [APEG, uncovered] | -0.2 | -19.2 |
| C-D | [APEG, uncovered] vs. [not treated, uncovered] | -63.7* | -46.4 |
| C-B | [APEG, uncovered] vs. [not treated, covered] | -44.1* | -36.6 |
| C-E | [APEG, uncovered] vs. [MPEG, uncovered] | -4.6 | -5.7 |
| E-D | [MPEG, uncovered] vs. [not treated, uncovered] | -59.2* | -40.7 |
| E-B | [MPEG, uncovered] vs. [not treated, covered] | -39.6 | -29.9 |
| B-D | [Not treated, covered] vs. [not treated, uncovered] | -19.6 | -10.8 |

* Difference is statistically significant, based on Tukey's pair-wise comparison procedure (overall significance level of 0.05).

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# APPENDIX A

# INDIVIDUAL TREATMENT NARRATIVE

# APPENDIX A
# INDIVIDUAL TREATMENT NARRATIVE

## A.1 TREATMENT #1: OCTOBER 15 - OCTOBER 21

### A.1.1 Inside Plots

Sample batch numbers DX000101 through DX000118, DX000201 through DX000218, and DX000301 through DX000314 were taken from the inside site. The first treatment was performed using concentrated APEG reagent that was poured uniformly over the plots designated as A and C. An attempt was made to pour the APEG using a watering can with a spray head attached. Due to the viscosity of the reagent, the spray head was removed and the reagent was poured directly onto the ground. It was allowed to puddle and was then raked into the soil using a standard three-pronged garden tool. The soil was well mixed in order to create an intimate contact between the soil particles and the reagent. After the substances were mixed, the plots were again raked and leveled and those plots designated within A were covered with a 5-foot by 5-foot square of black polyethene plastic.

The untreated plots labeled B and D were raked repeatedly to simulate the same mixing that was performed in the treated plots. Those labeled B were covered with polyethylene.

The E plots were poured with the MPEG, raked, and left exposed to the air. The general site area was cleaned up and the containers holding the sample bottles were carried to the transfer point for relay to the truck for packing prior to shipment.

Concurrent with the site preparation and prior to treatment, the soil moisture content was analyzed using a Speedy Moisture Meter. It was determined that the soil moisture ranged from 18 to greater than 21 percent.

In addition to plot samples, the bleacher planks inside the arena were surveyed to determine a spot that would have a sufficiently exposed surface without water marks caused by stable roof leaks. Four such sites were chosen. These were planks 30½-feet long by 9.6-feet wide and covered with a nonuniform coating of dust ranging from 1/16- to 1/8-inches deep. On two of these bleacher planks, dust was swept with a wisk broom and collected in sample bottles DX000315 and DX000316 for analysis. Treatment on the other two planks was delayed until the problem of application could be solved. Three field blanks DX000119, DX000219, and DX000317 were chosen off site at a point near the O.H. Materials, Inc., office. The samples were hand delivered to Envirodyne, St. Louis, for analysis.

A.1.2 Treatment 1: Outside Plot

The outside plot was identified by the EPA Project Officer, Charles Rogers, with the help of the former owner of Shenandoah Stables, Frank Hampel. Mr. Hampel was able to direct Mr. Rogers to the site where Mr. Hampel had disposed of the soil that was removed from the stable. The site was marked off as a 30-foot by 30-foot square. The undergrowth was cleared and the technician from O.H. Materials began an attempt to remove the protective overburden in order to uncover the original spoil materials. The overburden, consisting of a reddish-orange clay cap mixed with gravel, proved to be extremely resistant to shovels. After one shovel was broken, the Rototiller was brought on site to break the cover but this, too, proved to be unsuccessful. The site was relocated approximately 10 feet northwest of the original location.

At the new site, the soil was still resistant to penetration. However, continuous work with the Rototiller succeeded in providing enough penetration to allow shovels to work. It became evident that instead of 4 inches to 6 inches of clay cap, there were probably 12 inches to 18 inches. After 1½ days of work we were able to reach the original soil, indicated by a distinctive change in composition from clay to a compacted brown to black dirt.

During the work period, rain occurred. Since more rain was forecast it was evident that fully exposing the site in order to work during this trip would not be possible. Consequently, it was decided by the EPA project officer and the RTI project manager to delay further work on the outside plot until the next trip.

In the meantime, the soil taken from the plot was piled along the edges to prevent runoff from adjacent areas from entering the excavation and arrangements were made to cover the site with polyethylene plastic.

A shallow A-frame support was built over the site using a 2-inch by 4-inch timber as a central ridge pole and 2-inch by 4-inch timbers as stringers. The center line was located 1½ feet over the lip of the pit and the stringers were embedded in the top of the surrounding spoil-dirt. The site was then overlaid with clear polyethylene plastic with the side walls extended to cover the spoil-material. The edges were sandbagged and a rain gauge on site was installed on site to measure precipitation.

## A.2 TREATMENT 2: OCTOBER 30 - NOVEMBER 1

### A.2.1 Outside Plots

At the outside plots, the rain gauge showed that 1.4 inches of rain had fallen over the 9-day interim since the first visit. The outside plot was standing with water approximately 1-inch deep and covering over 60 percent of

the area at the bottom of the excavation. Since rainy, cold weather persisted, it was decided to abandon the outside plot until summer. The covering was reinforced and the sandbags relocated. Additional plastic was applied to preserve the site by O.H. Materials.

A.2.2 Inside Plots

At the inside plots, the sample bottles were labeled and distributed to each plot and the polyethylene covers were removed from the covered plots. It was discovered that moisture evaporating from the soil had condensed on the underside of the untreated and covered B plots. However, the treated and covered A plots were dry, indicating a hydroscopic potential for the APEG. Only the ground outside the A plots, where the cover had laid directly on the ground, showed moisture evaporation and condensation.

It was also observed that the A plots showed evidence of white deposits on the ground outside the frames that were immediately adjacent to the plots. It was assumed that this was a salt deposit formed by salt being deposited at the soil surface as water was being drawn into the APEG reagent. Much later, on the third treatment, it was discovered that this was a white filamentous growth, perhaps a mold or fungus, that was able to colonize in the area under the cover.

The treated plots showed a slight marbling effect, indicating the interface between the treated and untreated soil. It was evident that, due to the viscosity of the APEG, a 100-percent uniform application during the first treatment had not been achieved.

The overall treatment plan was modified by the EPA project officer to facilitate the application of the APEG reagent. At his direction, the APEG was mixed as a 2 to 1 ratio of toluene to APEG. A clean 55-gallon barrel with

a valve and spout was supplied by O.H. Materials for mixing. The toluene and APEG was poured directly into the drum, stirred, and capped off. Our previous laboratory work had shown that APEG would not separate from the toluene once mixed.

The MPEG was not diluted on this treatment due to a shortage of toluene. Consequently, in this test the MPEG was brought in directly from the truck via spray cans. Due to the relatively low viscosity, MPEG did not present a problem in pouring.

The samples were taken using the same guidelines as established in the protocol. Acetate tubes were used to collect the samples from the untreated plots; they were disposed of after compositing one sample. Stainless steel tubes were used to collect the treated samples. One tube per sample was used and then placed in water to soak until it would be washed prior to its next use.

Fifty plot samples were collected from the plot and three additional background samples, DX000420, DX000521, and DX000612, were collected from the southwest corner of the stable area. This change was made at the direction of the project officer out of a concern to have the background samples be as identical as possible to the arena sample matrix.

In addition to the plot and background samples, other samples were taken to characterize the soil surrounding the outside plot such as DX000522 and DX000523. These samples were taken approximately 15 feet to the rear of the outside plot at a point midway between the plot and the slough. Debri, 2- or 3-inches thick of dead vegetation, was removed in order to get to the soil surface. A 6-inch-deep sample was taken using a garden trowel and placed in a

labeled jar. Earth worms were observed in the hole where the sample had been taken.

One other sample was taken from the spoil-material that was turned over during the excavation of the outside plot. Sample DX000524 was taken on the left side of the plot at a point midway between the front and rear of the spoil mound on the side nearest the road. This was done from an area left open during the cover-up. The sample consisted of a mixture of dark soil and normal-looking clay. A layer of this mixture approximately 2- to 3-inches thick was taken off the surface and placed in a bottle.

The plots were treated with the toluene-APEG mixture. This mixture was found to have superior pour characteristics to those of straight APEG. The spray caps were secured on the spray cans and a uniform distribution was applied over the plot. The plots were treated and allowed to soak for approximately 5 minutes before the soil was stirred once again. After the treatment, Plots A and D were recovered and samples were shipped to Geochemical, Houston, Texas.

A.3 TREATMENT 3: NOVEMBER 14 - NOVEMBER 16

The rain gauge indicated that 2.5 inches of rain had fallen on the site in the interim since Treatment 2. Also, during this interim, O.H. Materials had returned to the site to reinforce the plastic covering and to seal the open end.

A.3.1 Outside Plot

The plastic covering on the outside plot was showing the stress of accumulated rainwater. The stringers were beginning to buckle under the weight of the water. The periphery of the site was re-covered and sandbags were adjusted to hold the cover in place.

A.3.2 Inside Plot

Another 55-gallon drum was moved on site for the MPEG-toluene mixture. A standard agricultural pump-spray was purchased from a local farm supply store to be used in spraying the bleacher planks.

The plots were again uncovered and moisture accumulations were again noted on the untreated and covered plots; there was no evidence of moisture on either. In addition, the white patches under the A plots had reached sufficient density to allow them to be identified as being living organisms rather than as being an inert salt accumulation.

One other phenomena was noted: the presence of a substantial number of millipedes on the surface of the treated and uncovered C plots; they were alive, but immobile. Only one other plot, with MPEG control, contained such creatures and in lesser numbers.

The plots were sampled, sprayed, and covered. The bleacher planks were also sprayed using the pump-spray. A nonuniform application of 1½ gallons over the test area of 30½ by 9.6 feet was carried out. Unfortunately, the sprayer did not perform consistently well, apparently due to the rapid evaporation of the toluene and the residue left by the APEG.

The plot samples were DX000701 through DX000717, DX000801 through DX000817, and DX000901 through DX000916. Sample numbers DX000718, DX000818, and DX000917 were taken as field blanks at the previous designated area.

Other samples were taken from outside the stable. DX000918 was taken inside the outside plot perimeter at a point approximately 18 inches outside and on the center line. DX000918 was taken at a point approximately 3 feet from the center point of the horse walker area at a point closest to the outside plot. Sample DX000920 was taken as a surface sample in the designated clean-up area on the "safe" side of the fence.

A.4 TREATMENT 4: NOVEMBER 28 - NOVEMBER 30

The rain gauge indicated that 2.3 inches of rain had fallen on the site during the interim between visits. The outside plots were holding water but generally, were in good shape as far as the plastic cover was concerned. Tire and boot tracks as well as a horse trailer newly located at the stable indicated that there were other people using the site.

A.4.1 Inside Plot

The inside plots were uncovered and moisture accumulations were again noted. The growth of fungus had progressed to form a visibly fluffy white cotton-like mass. The last sample jars were then spread out and ready for transport.

In addition to sampling, we had been directed by the EPA project officer to take temperature readings during the visit. Two indoor/outdoor thermometers were installed in an untreated, uncovered plot to record temperature readings. (See Figure A.1). The thermometers were standard indoor/outdoor household instruments containing mercury bulbs to measure inside air temperature and a thermocouple to measure outside air temperature. The thermocouple was used as a soil probe; one was buried approximately ½ inch below the soil surface to reveal the surface temperature; the other one was buried approximately 1½ inches below the surface to measure the deeper temperature. Since the thermometers were not calibrated they could only give an approximate reading. Still, a very good temperature comparison between the two was accomplished.

The data indicates that during the night the soil most likely reaches the ambient air temperatures that one would expect to reach in shallow soil. When the sun rises and metal buildings heat up, the air temperature rises fairly rapidly. This rise is paralleled by the soil temperature. However, a deeper

probe shows that the lower layers are cooler than the upper layers, indicating the expected temperature gradient.

The regular set of samples DX0001001 through DX0001019, DX001101 through DX00101119, and DX0001201 through DX0001212 were taken from the plots. Field blanks DX0001213, DX0001214, DX0001215 were taken from the designated blank area. In addition, the blanks were split using DX0001218, and DX0001219, in order to serve as a cross-check on the dioxin background.

The bleacher planks were sampled using DX0001216 as a sample on the higher plank from Treatment area 1 and DX0001217 from the lower planks at Treatment area number 2. The bleacher samples were taken using a paint scraper. The paint scraper was held at a 45° angle and pushed along the surface of the bleacher plank rolling up a continuous ribbon of mud and paint. The ribbons were then placed into a sample bottle and shaken in an attempt to homogenize the sample. However, that did not work and the sample remained essentially intact.

Since this was the last proposed treatment for this period, the site was checked to be sure that all of the debri was bagged and placed at the front of the stable. In order to facilitate a long-term check, the plot was re-covered as though there were a test in progress. Contaminated equipment was boxed, taped, labeled "Dioxin", and placed at the site.

The final batches were shipped out. Batch number 11 and 12 (DX0001100 and DX0001200) were sent to ETC in New Jersey for analysis; batch number 10 (DX0001000) was sent to Geochemical in Houston, Texas.

1. ½ inch below ground surface:

| 28 November | | | 29 November | |
|---|---|---|---|---|
| Time | Soil | Air | Soil | Air |
| 9:20 | | | 42 | 38 |
| 10:00 | | | 44 | 44 |
| 10:30 | | | 44 | 46 |
| 11:00 | | | -- | -- |
| 11:30 | | | 45 | 48 |
| 12:00 | | | 48 | 52 |
| 12:30 | | | 48 | 54 |
| 1:00 | | | -- | -- |
| 1:30 | 49 | 49 | -- | -- |
| 2:00 | -- | -- | -- | -- |
| 2:30 | 49 | 49.5 | -- | -- |
| 3:00 | -- | -- | -- | -- |
| 3:30 | 48 | 48 | -- | -- |

2. 1½ inches below ground surface

| 28 November | | | 29 November | |
|---|---|---|---|---|
| Time | Soil | Air | Soil | Air |
| 9:20 | | | 38 | 38 |
| 10:00 | | | 40 | 40 |
| 10:30 | | | 42 | 44 |
| 11:00 | | | -- | -- |
| 11:30 | | | 43 | 46 |
| 12:00 | | | 48 | 51 |
| 12:30 | | | 48 | 55 |
| 1:00 | | | -- | -- |
| 1:30 | 48 | 49 | -- | -- |
| 2:00 | -- | -- | -- | -- |
| 2:30 | 48.5 | 49.5 | -- | -- |
| 3:00 | -- | -- | -- | -- |
| 3:30 | 47 | 48 | -- | -- |

Figure A.1. Temperature readings (°F): Inside plot.

# APPENDIX B

# SAMPLE MANAGEMENT OFFICE (SMO)

# ANALYTICAL PROCEDURES

# ANALYTICAL METHODS

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## Exhibit D - Analytical Methods

### 2,3,7,8-tetrachlorodibenzo-p-dioxin in Soil and Sediment by High Resolution Gas Chromatography/ Low Resolution Mass Spectrometry

1. SCOPE AND APPLICATION

1.1 This method provides procedures for detection and measurement of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD; CAS Registry Number 1746-01-6; STORET Number 34675) at concentrations of 1 $\mu$g/kg to 200 $\mu$g/kg in 10-g aliquots of wet soil and sediment. The use of 1-g aliquots permits measurement of concentration up to 2000 $\mu$g/kg.

1.2 The minimum measurable concentration is estimated to be 0.3 $\mu$g/kg, but is dependent on interfering compounds present in the sample matrix.

1.3 This method is designed for use by analysts who are experienced in the use of a gas chromatograph/mass spectrometer.

1.4 CAUTION: Because 2,3,7,8-TCDD is extremely toxic, safety procedures described in Section 5 of this method should be followed to prevent exposure of laboratory personnel to materials containing this compound.

2. SUMMARY OF METHOD

After 50 ng of $^{13}C$-labeled 2,3,7,8-TCDD and 10 ng of $^{37}Cl$-labeled 2,3,7,8-TCDD are added to a 10 gram aliquot of soil or sediment sample, the wet soil or sediment is mixed with 20 grams of anhydrous sodium sulfate and is extracted with a mixture of hexane and methanol, while the sample aliquot and solvent are agitated continually in a glass jar. Column chromatographic procedures are used to help eliminate sample components that may interfere with detection and measurement of 2,3,7,8-TCDD. The extract is concentrated to 50 $\mu$L, and a 2 $\mu$L aliquot is injected into a fused silica capillary column in a gas chromatograph (GC) interfaced to a mass spectrometer (MS) that has at least unit resolution at m/z 334.

Identification of 2,3,7,8-TCDD is based on detection of three characteristic ions, measurement of the appropriate relative abundances of two characteristic ions in the molecular ion cluster, and determination of the retention time of the sample analyte relative to the internal standard, $^{13}C_{12}$-2,3,7,8-TCDD, contained in the sample extract. The 2,3,7,8-TCDD concentration is determined by measuring the MS response to the sample component relative to the MS response to $^{13}C_{12}$-2,3,7,8-TCDD (the internal standard). The labeled internal

standard method presumes that internal standard losses during method procedures are equal to unlabeled TCDD losses. Therefore, the calculated sample 2,3,7,8,-TCDD concentration is corrected for losses during sample preparation.

The $^{37}Cl_4$-2,3,7,8- TCDD is a surrogate compound that is added to each sample and is analyzed exactly the same as unlabeled TCDD. The accuracy of surrogate compound measurement is used to indicate the accuracy of measurement of unlabeled 2,3,7,8-TCDD in the same sample.

## 3. DEFINITIONS

3.1 Concentration calibration solution -- a solution containing known amounts of the analyte (unlabeled 2,3,7,8-TCDD), the surrogate compound ($^{37}Cl_4$-2,3,7,8-TCDD), and the internal standard ($^{13}C_{12}$-2,3,7,8-TCDD); it is used to determine instrument response of the analyte and the surrogate compound relative to the internal standard.

3.2 Field blank -- a portion of soil/sediment uncontaminated with 2,3,7,8-TCDD.

3.3 Rinsate -- a portion of solvent used to rinse sampling equipment and analyzed to demonstrate that samples are not contaminated during sampling.

3.4 Internal standard -- $^{13}C_{12}$-2,3,7,8-TCDD, which is added to every sample and is present at the same concentration in every blank, quality control sample, and concentration calibration solution. It is added to the soil/sediment sample before extraction and is used to measure the concentrations of analyte and surrogate compound.

3.5 Laboratory reagent blank -- a blank prepared by the laboratory by performing all analytical procedures except addition of a sample aliquot to the extraction vessel.

3.6 Performance check mixture -- a mixture of known amounts of selected standard compounds; it is used to demonstrate continued acceptable performance of the GC/MS/DS system.

3.7 Performance evaluation sample -- a soil or sediment sample containing a known amount of unlabeled 2,3,7,8-TCDD. It is distributed by EPA to potential contractor laboratories who must analyze it and obtain acceptable results before being awarded a contract for sample analyses (see IFB Pre-Award Bid Confirmations). It may also be included as an unspecified QC sample in any sample batch submitted to the lab for analysis.

3.8 Response factor -- response of the mass spectrometer to a known amount of an analyte relative to a known amount of an internal standard.

3.9 Signal-to-noise ratio -- The ratio of the area of the analyte signal to the area of the random background signal; it is determined by integrating the signal for a characteristic ion in a region of the selected ion current profile where only random noise is observed and relating that area to the area measured for a positive response for the same ion. The same number of spectra must be integrated for both areas. (The ratio of peak heights may be used instead of peak areas.)

3.10 Surrogate compound -- $^{37}Cl_4$-2,3,7,8-TCDD, which is added to the soil/sediment before analysis. Its concentration is measured in each sample, and the accuracy of that concentration measurement is calculated to indicate the accuracy of the unlabeled 2,3,7,8-TCDD measurement.

## 4. INTERFERENCES

Any organic compound that is within 10 scans (at the rate of 1 scan/second) of m/z 257, 320, 322, or 328 of the internal standard and produces any of the three ions monitored to detect 2,3,7,8-TCDD, is a potential interference. Most frequently encountered interferences are other sample components that are extracted along with TCDD. Because very low levels of TCDD must be measured, elimination of interference is essential. High purity reagents and solvents must be used and all equipment must be scrupulously cleaned. Laboratory reagent blanks (Exhibit E, Quality Control, Section 4) must be analyzed to demonstrate lack of contamination that would interfere with TCDD measurement. Column chromatographic procedures are used to remove some coextracted sample components; these procedures must be performed carefully to minimize loss of TCDD during attempts to enrich its concentration relative to other sample components.

## 5. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a file of current OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are identified.[1-3] 2,3,7,8-TCDD has been identified as a suspected human or mammalian carcinogen.

5.2 Each laboratory must develop a strict safety program for handling 2,3,7,8-TCDD. The following laboratory practices are recommended:

5.2.1 Contamination of the laboratory will be minimized by conducting all manipulations in a hood.

5.2.2 The effluents of sample splitters for the gas chromatograph and roughing pumps on the GC/MS should pass through either a column of activated charcoal or through a trap containing oil or high-boiling alcohols.

5.3 The following precautions for safe handling of 2,3,7,8-TCDD in the laboratory are presented as guidelines only, and are based on safe handling practices included in USEPA Method 613.(4) The precautions for safe handling and use are necessarily general in nature because detailed, specific recommendations can be made only for the particular exposure and circumstances of each individual usage. Assistance in evaluating the health hazards of particular laboratory conditions may be obtained from certain consulting laboratories and from State Departments of Health or of Labor, many of which have an industrial health service. Although 2,3,7,8-TCDD is extremely toxic to laboratory animals, it has been handled for years without injury in analytical and biological laboratories. Techniques used in handling radioactive and infectious materials are applicable to 2,3,7,8-TCDD.

5.3.1 Protective Equipment: Throw-away plastic gloves, apron or lab coat, safety glasses and lab hood adequate for radioactive work.

5.3.2 Training: Workers must be trained in the proper method of removing of contaminated gloves and clothing without contacting the exterior surfaces.

5.3.3 Personal Hygiene: Thorough washing of hands and forearms after each manipulation and before breaks (coffee, lunch, and shift) with any mild soap and plenty of scrubbing action.

5.3.4 Confinement: Isolated work area, posted with signs; segregated glassware and tools; and plastic-backed absorbent paper on benchtops.

5.3.5 Waste: Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans. Janitors should not handle wastes.

5.3.6 Disposal of Wastes: 2,3,7,8-TCDD decomposes above 800°C. Low level waste, such as the absorbent paper and plastic gloves, may be burned in a good incinerator. Water containing gross quantities (milligrams) of 2,3,7,8-TCDD should be packaged securely and disposed through commercial or governmental channels that are capable of handling

high-level or extremely toxic wastes. Liquids should be allowed to evaporate in a good hood and in a disposable container; residues may then be handled as above.

5.3.7 Glassware, Tools, and Surfaces: Satisfactory cleaning may be accomplished by rinsing with 1,1,1-trichloroethane, then washing with any detergent and water. Dishwater may be disposed to the sewer. (Also see Section 6.5.)

5.3.8 Laundry: Clothing known to be contaminated should be disposed with the precautions described under Section 5.3.6. Lab coats or other clothing worn in 2,3,7,8-TCDD work may be laundered. Clothing should be collected in plastic bags. Persons who convey the bags and launder the clothing should be advised of the hazard and trained in proper handling. The clothing may be put into a washer without contact if the launderer knows the problem. The washer should be run through a cycle before being used again for other clothing. Disposable garments may be used to avoid a laundry problem, but they must be properly disposed or incinerated.

5.3.9 Wipe Tests: A useful method to determine cleanliness of work surfaces and tools is to wipe the surface with a piece of filter paper, which is extracted and analyzed by gas chromatography (limit of sensitivity of approximately 0.1 $\mu$g per wipe). Less than 0.1 $\mu$g 2,3,7,8-TCDD per wipe indicates acceptable cleanliness; anything higher warrants further cleaning. More than 10 $\mu$g on a wipe sample indicates an acute hazard that requires prompt cleaning before further use of the equipment or work space and indicates that unacceptable work practices have been employed in the past.

5.3.10 Inhalation: Any procedure that may produce airborne contamination must be performed with good ventilation. Gross losses to a ventilation system must not be allowed. Handling of the dilute solutions normally used in analytical and animal work presents no inhalation hazards except in case of an accident. Finely divided soils contaminated with 2,3,7,8-TCDD are hazardous because of the potential for inhalation. Such samples should be handled in a confined environment, such as a hood or glove box, or laboratory personnel should wear masks fitted with a particulate filter and charcoal sorbent.

5.3.11 Accidents: Remove contaminated clothing immediately, taking precautions not to contaminate skin or other articles. Wash exposed skin vigorously and repeatedly until medical attention is obtained.

## 6. APPARATUS AND EQUIPMENT

### 6.1 Gas Chromatograph/Mass Spectrometer/Data System (GC/MS/DS)

6.1.1 The GC must be capable of temperature programming and be equipped with all required accessories, such as syringes, gases, and a capillary column. The GC injection port must be designed for capillary columns. Splitless or on-column injection technique is recommended. With this method, a 2-$\mu$L injection volume is used consistently. With some GC injection ports, however, 1 $\mu$L may be the maximum volume that produces adequate precision and chromatographic separation. A 1-$\mu$L injection volume may be used if adequate sensitivity and precision can be achieved. CAUTION: If 1 $\mu$L is used for any injection volume, the injection volume for all extracts, blanks, calibration solutions and the performance check sample must be 1 $\mu$L.

6.1.2 Mass spectral data are obtained with electron ionization at a nominal electron energy of 70 eV. To ensure sufficient precision of mass spectral data, the required MS scan rate must allow acquisition of at least five data points for each of six ions while a sample component elutes from the GC.

6.1.3 An interfaced data system (DS) is required to acquire, store, reduce and output mass spectral data. The DS must be equipped with a selected ion monitoring (SIM) program to acquire data for at least six ions that are characteristic of labeled and unlabeled 2,3,7,8-TCDD. (The mass spectrum of unlabeled 2,3,7,8-TCDD is shown in Figure 1 at the end of this Exhibit.) The same integration time must be used for each ion monitored, and the integration time used for sample analyses must be the same as the time used to analyze concentration calibration solutions and the performance check solution. Total data acquisition time per cycle (six ions) must not exceed 1.5 seconds.

6.2 GC Column -- Two fused silica capillary columns are recommended; one is a 60-m SP-2330 and the other is a 50-m CP-SIL 88. Any capillary column that separates 2,3,7,8-TCDD from all other TCDDs may be used, but this separation must be demonstrated. Minimum acceptance criteria must be determined per Section 9.2.3.1. At the beginning of each 8-hour period during which sample or concentration calibration solutions will be analyzed, column operating conditions must be demonstrated to achieve the required separation on the column to be used for samples. Operating conditions known to produce acceptable results with the recommended columns are shown in Table 1 at the end of this Exhibit.

6.3 Miscellaneous Equipment

6.3.1 Nitrogen evaporation apparatus with variable flow rate from approximately 30 mL/min to 150 mL/min.

6.3.2 Mechanical shaker -- A magnetic stirrer or a wrist-action or platform-type shaker that produces vigorous agitation. Agitation conditions must be determined and demonstrated.

6.3.3 Analytical balance capable of accurately weighing 0.01g.

6.3.4 Centrifuge capable of operating at 2000 rpm.

6.3.5 Water bath -- equipped with concentric ring cover and temperature controlled within ± 2°C.

6.3.6 Stainless steel spatulas or spoons.

6.3.7 Stainless steel (or glass) pan large enough to hold contents of 1-pint sample containers.

6.3.8 Glove box.

6.4 Glassware

6.4.1 Extraction jars -- amber glass with Teflon-lined screw cap; minimum capacity of approximately 500 mL; must be compatible with mechanical shaker to be used.

6.4.2 Kuderna-Danish apparatus -- 500-mL evaporating flask, 10-mL graduated concentrator tubes with ground-glass stoppers, and 3-ball macro Snyder column.

6.4.3 Culture tubes -- 8-mL glass.

6.4.4 Mini-vials -- 1-mL amber borosilicate glass with conical-shaped reservoir and screw caps lined with Teflon-faced silicone disks.

6.4.5 Funnels -- glass; appropriate size to accommodate filter paper used to filter jar extract (volume of approximately 170 mL).

6.4.6 Chromatography columns -- 1 cm ID x 10 cm long and 1 cm ID by 30 cm long.

6.5 NOTE: Reuse of glassware should be minimized to avoid the risk of using contaminated glassware. All glassware that is reused must be scrupulously cleaned as soon as possible after use, applying the following procedure.

Rinse glassware with the last solvent used in it. Wash with hot water containing detergent. Rinse with copious amounts of tap water and several portions of distilled water. Drain dry and heat in a muffle furnace at 400°C for 15 to 30 min. Volumetric glassware should not be heated in a muffle furnace, and some thermally stable materials (such as PCBs) may not be removed by heating in a muffle furnace. In these cases, rinsing with high-purity acetone and hexane may be substituted for muffle furnace heating. After glassware is dry and cool, store inverted or capped with aluminum foil in a clean environment.

## 7. REAGENTS AND CONSUMABLE MATERIALS

### 7.1 Column Chromatography Reagents

7.1.1 Alumina, acidic -- Soxhlet extract with methylene chloride for 21 hours and activate by heating in a foil covered glass container for 24 hours at 190°C.

7.1.2 Silica gel -- high purity grade, type 60, 70-230 mesh; Soxhlet extract with methylene chloride for 21 hours and activate by heating in a foil-covered glass container for 24 hours at 130°C.

7.1.3 Silica get impregnated with sodium hydroxide -- Add one part of 1 M NaOH solution to two parts of silica in a screw cap bottle and mix with a glass rod until free of lumps.

7.1.4 Silica gel impregnated with 40% (by weight) sulfuric acid -- Add two parts (by weight) concentrated sulfuric acid to three parts (by weight) silica gel (extracted and activated), mix with a glass rod until free of lumps, and store in a screw-capped glass bottle.

7.1.5 Sulfuric acid, concentrated -- ACS grade, specific gravity 1.84.

7.1.6 Graphitized carbon black (Carbopack C or equivalent), surface area of approximately 12 $m^2/g$, 80/100 mesh.

7.1.7 Celite 545$^R$, reagent grade, or equivalent.

7.2 Filter paper -- pore size of $\leq$ 20 to 25 ug; rinse with hexane before use.

7.3 Glass wool, silanized -- Extract with methylene chloride and hexane before use.

7.4 Sodium sulfate -- Granular, anhydrous; before use, extract with methylene chloride and dry for $\geq$ 4 h in a shallow tray placed in an oven operated at 120°C.

7.5 Solvents -- High purity, distilled-in-glass; hexane, methanol, methylene chloride, and toluene.

7.6 Concentration Calibration Solutions (reference Table 2) -- Five toluene solutions containing unlabeled 2,3,7,8-TCDD at varying concentrations and $^{13}C_{12}$-2,3,7,8-TCDD (the internal standard, CASRN 80494-19-5) at a constant concentration. Three of these solutions also contain $^{37}Cl_4$-2,3,7,8-TCDD (the surrogate compound, CASRN 85508-50-5) at varying concentrations. Concentration calibration solutions are to be obtained from the Quality Assurance Division, USEPA Environmental Monitoring Systems Laboratory (EMSL-LV), Las Vegas, Nevada. However, if not available from EMSL-LV, standards may be obtained from commercial sources, and solutions may be prepared in the contractor laboratory. Traceability of standards must be verified against EPA-supplied standard solutions, by laboratory SOP's as required in IFB Pre-Award Bid Confirmations, part 2.f.(4).

7.6.1 Each of solutions #1-#5 contains $^{13}C_{12}$-2,3,7,8-TCDD at a concentration of 1 ng/uL which is equivalent to a 50-uL extract of a 10-g sample to which that compound (the internal standard) was added at a concentration of 5 ug/kg.

7.6.2 Solutions #1-#5 contain unlabeled 2,3,7,8-TCDD at concentrations of 0.2, 1, 5, 20 and 40 ng/uL respectively; those concentrations are equivalent to 50-uL extracts of 10-g samples containing 1, 5, 25, 100 and 200 ppb, respectively.

7.6.3 Solutions #1-#3 contain $^{37}Cl_4$-2,3,7,8-TCDD at concentration of 0.06, 0.12, and 0.2 ng/uL, respectively; those concentrations are equivalent to extracts containing 30%, 60%, and 100%, respectively, of the amount of $^{37}Cl_4$-TCDD (the surrogate compound) added to each sample before extraction.

7.6.4 Store concentration calibration solutions in 1-mL amber mini-vials at room temperature.

7.7 Performance Check Solution -- A mixture containing: unlabeled 2,3,7,8-TCDD; 1,2,3,4-TCDD (CASRN 30746-58-8); 1,4,7,8-TCDD (CASRN 40581-94-0); 1,2,3,7-TCDD (CASRN 67028-18-6); 1,2,3,8-TCDD (CASRN 53555-02-5); 1,2,7,8-(CASRN 34816-53-0) and 1,2,6,7-TCDD (CASRN 40581-90-6) must be obtained from the Quality Assurance Division, Environmental Monitoring Systems Laboratory, Las Vegas, Nevada.

To this dry mixture add 500 uL of the sample fortification solution (Section 7.8) containing $^{13}C_{12}$-2,3,7,8-TCDD at a concentration of 0.5 ng/uL and $^{37}Cl_4$-2,3,7,8-TCDD at a concentration of 0.1 ng/uL. Store in 1-mL amber mini-vial at room temperature.

7.8 Sample Fortification Solution - a toluene solution containing the internal standard at a concentration of 0.5 ng/$\mu$L and the surrogate compound at a concentration of 0.1 ng/$\mu$L.

7.9 Field Blank Fortification Solution - a toluene solution containing the internal standard at a concentration of 0.5 ng/$\mu$L, the surrogate compound at a concentration of 0.1 ng/$\mu$L, and the unlabeled 2,3,7,8-TCDD at a concentration of 0.1 ng/$\mu$L.

8. SAMPLE PRESERVATION AND HANDLING

8.1 Chain-of-custody procedures -- see Exhibit C.

8.2 Sample Preservation

8.2.1 When received, each sample will be contained in a 1-pint glass jar surrounded by vermiculite in a sealed metal paint can. Until a portion is to be removed for analysis, store the sealed paint cans in a locked limited-access area where ambient temperature is maintained between 0°C and 35°C. After a portion is removed for analysis, return the unused portion of sample to its original containers and store as stated above. Do not freeze samples; they may contain sufficient water to break the sample jar if frozen.

8.2.2 To avoid photodecomposition, protect samples from light.

8.3 Sample Handling

8.3.1 CAUTION: Finely divided soils contaminated with 2,3,7,8-TCDD are hazardous because of the potential for inhalation or ingestion of particles containing 2,3,7,8-TCDD. Such samples should be handled in a confined environment (i.e., a closed hood or a glove box).

8.3.2 Pre-extraction sample treatment

8.3.2.1 Homogenization -- Although sampling personnel will attempt to collect homogeneous samples, the contractor shall examine each sample and judge if it needs further mixing. NOTE: Contractor personnel have the responsibility to take a representative sample aliquot; this responsibility entails efforts to make the sample as homogeneous as possible. Stirring is recommended when possible.

8.3.2.2 Centrifugation -- If a sample contains an obvious aqueous/liquid phase, centrifuge it to separate liquid and solid phases. Place the entire sample in a suitable centrifuge bottle and centrifuge for 30

minutes at 2000 rpm. Remove bottle from centrifuge. With a disposable pipet, remove liquid phase and discard. CAUTION: This liquid may contain TCDD and should be disposed as a liquid waste. Mix solid layer with stainless steel spatula and remove a portion to be weighed and analyzed. Return the remaining solid portion to original sample bottle and store.

## 9. CALIBRATION

9.1 Two types of calibration procedures are required. One type, routine calibration, is required at the beginning and end of each 8-hour period during which TCDD analyses are performed. The other type, initial calibration, is required before any samples are analyzed for TCDD, and is required intermittently throughout sample analyses as dictated by results of routine calibration procedures described below. No samples are to be analyzed until acceptable calibration is demonstrated and documented.

9.2 Routine Calibration

9.2.1 Calibrate and tune the MS with standards and procedures prescribed by the manufacturers. CAUTION: Some manufacturers may specify baseline resolution at masses higher than necessary for this method; that procedure could significantly reduce sensitivity for TCDD analysis.

9.2.2 Inject 2 $\mu$L (CAUTION: See Sect. 6.1.1) of the performance check solution (Sect. 7.7) and acquire selected-ion-monitoring mass spectral data for m/z 320, 322, 323, 328, 332, and 334 within a total cycle time of $\leq$ 1.5 seconds. Acquire at least five data points for each GC peak and use the same data acquisition time for each of the six ions being monitored. NOTE: The same data acquisition parameters previously used to analyze concentration calibration solutions during initial calibration must be used for the performance check solution.

9.2.3 Determine and document acceptable system performance with the following criteria:

9.2.3.1 GC column performance -- If SP-2330 column is used, the valley between 2,3,7,8-TCDD and the peaks representing all other TCDD isomers must be resolved with a valley $\leq$ 25%. Valley (%) = x/y X 100, when y is peak height of 2,3,7,8-TCDD; x is measured as shown in Figures 2 and 3 at the end of this Exhibit . The peak representing 2,3,7,8-TCDD shall be labeled and identified as such on the chromatograms.

9.2.3.2 Ratio of integrated ion current for m/z 320 to m/z 322 for 2,3,7,8-TCDD must be $\geq$ 0.67 and $\leq$ 0.87.

9.2.3.3 MS resolution -- Ratio of integrated ion current for m/z 323 relative to m/z 322 for unlabeled 2,3,7,8-TCDD should be $\geq$ 0.07 and $\leq$ 0.20.

9.2.3.4 Ratio of integrated ion current for m/z 332 to m/z 334 for $^{13}C_{12}$-2,3,7,8-TCDD must be $\geq$ 0.67 and $\leq$ 0.87.

9.2.3.5 Response factor (Sect. 9.3.10) for $^{37}Cl_4$-2,3,7,8-TCDD relative to $^{13}C_{12}$-2,3,7,8-TCDD must be within $\pm$ 10% of the mean value established by triplicate analyses of the concentration calibration solutions (Section 9.3).

9.2.4 Inject 2 $\mu$L of the concentration calibration solution #1, which contains 0.2 ng/$\mu$L of unlabeled 2,3,7,8-TCDD. Using the same GC/MS/DS conditions as used in Section 9.2.2 except the ions being monitored, acquire data for m/z 257, 320, 322, 328, 332, and 334. Determine and document acceptable performance for:

9.2.4.1 MS sensitivity -- signal-to-noise (S/N) ratio (Section 3.8) of $\geq$ 2.5 for m/z 257 and $\geq$ 10 for m/z 322 for unlabeled 2,3,7,8-TCDD. The ratio of integrated ion current for m/z 257 to m/z 322 must be $\geq$ 0.20 and $\leq$ 0.45.

9.2.4.2 Measured response factor for unlabeled 2,3,7,8-TCDD relative to $^{13}C_{12}$-2,3,7,8-TCDD is within $\pm$ 10% of the mean values established (Section 9.3) by triplicate analyses of the concentration calibration solutions.

9.2.5 Remedial actions shall be taken by Contractor if criteria are not met. Possible remedies are:

9.2.5.1 Check and adjust GC and/or MS operating conditions.

9.2.5.2 Replace GC column (performance of initial calibration procedures then required).

9.2.5.3 Tune MS for greater or lesser resolution.

9.2.5.4 Calibrate MS mass scale.

9.2.5.5 Prepare and analyze new performance check solution.

9.2.5.6 Prepare new concentration calibration curve(s) (Section 9.3.11).

9.3 Initial Calibration

9.3.1 In addition to routine calibration procedures described in Section 9.2, before any samples are analyzed, determine response factors for $^{37}Cl_4$-2,3,7,8-TCDD and for unlabeled 2,3,7,8-TCDD relative to $^{13}C_{12}$-2,3,7,8-TCDD.

9.3.2 Concentration calibration solutions -- The five solutions described in Section 7.6 are required.

9.3.3 Calibrate and tune the MS with standards and procedures prescribed by the instrument manufacturer.

9.3.4 If a column other than the recommended (Section 6.2) SP-2330 or CP-SIL 88 fused silica capillary column is used, determine the GC conditions necessary to separate 2,3,7,8-TCDD from other TCDDs known to have similar relative retention times.

9.3.5 Inject a 2-$\mu$L aliquot of the performance check solution (CAUTION: See Section 6.1.1) and acquire selected-ion-monitoring (SIM) mass spectral data using the MS operating conditions specified in Section 9.2.2. Determine GC operating conditions necessary to achieve separation described in Section 9.2.3.1.

9.3.6 Using specified MS data acquisition procedures and the GC conditions determined in Section 9.3.5, analyze a 2-$\mu$L aliquot of the performance check solution.

9.3.7 Determine and document acceptable calibration using the criteria specified in Section 9.2.3.1 - 9.2.3.5.

9.3.8 Using the same GC conditions that produced acceptable results with the performance check solution, analyze a 2-$\mu$L aliquot of each of the five concentration calibration solutions with the following MS operating parameters.

9.3.8.1 Acquire selected-ion-monitoring data for m/z 257, 320, 322, 328, 332 and 334.

9.3.8.2 Total cycle time for data acquisition must be $\leq$ 1.5 seconds.

9.3.8.3 Acquire at least five data points for each ion during elution of the GC peak.

9.3.8.4 Use the same data acquisition time for each of the six ions being monitored.

9.3.9 Repeat Section 9.3.8 two times to produce triplicate data sets for each solution.

9.3.10 Calculate the response factor for $^{37}Cl_4$-2,3,7,8-TCDD and for unlabeled 2,3,7,8-TCDD relative to $^{13}C_{12}$-2,3,7,8-TCDD:

$$RF = \frac{A_x \cdot Q_{is}}{A_{is} \cdot Q_x}$$

where $A_x$ = integrated ion abundance (corrected as specified in Section 12.1.1.3) of m/z 328 for $^{37}Cl_4$-2,3,7,8,-TCDD or the sum of integrated ion abundances of m/z 320 and m/z 322 for unlabeled 2,3,7,8-TCDD,

$A_{is}$ = the sum of integrated abundances of m/z 332 and m/z 334 for $^{13}C_{12}$-2,3,7,8-TCDD,

$Q_{is}$ = quantity of $^{13}C_{12}$-2,3,7,8-TCDD, and

$Q_x$ = quantity of unlabeled 2,3,7,8-TCDD or $^{37}Cl_4$-2,3,7,8-TCDD injected.

RF is a unitless number; units used to express quantities must be equivalent.

9.3.11 For both $^{37}Cl_4$-2,3,7,8-TCDD and unlabeled 2,3,7,8-TCDD, calculate the mean RF and its relative standard deviation (RSD) from triplicate analyses of each of the five concentration calibration solutions. Variation of the RF calculated for each compound at each concentration level must not exceed 10% RSD. If the five mean RFs for each compound do not differ by more than $\pm$ 10%, the RF can be considered to be independent of analyte quantity for the calibration concentration range, and the mean of the five mean RFs shall be used for concentration calculations.

## 10. QUALITY CONTROL

See Exhibit E for QA/QC Requirements.

## 11. PROCEDURES

### 11.1 Sample Extraction

11.1.1 CAUTION: See Section 5 for safety guidelines and recommendations.

11.1.2 Jar extraction. NOTE: Extremely wet samples may require centrifuging to remove water before addition of sodium sulfate see (Section 8.3.2.2).

11.1.2.1 Accurately weigh to three significant figures a 10 gram (± 0.5 gram) portion of the wet soil or sediment sample, and transfer it to the extraction jar.

11.1.2.2 Add 100 µL of the sample fortification solution (Section 7.8) to the soil or sediment in the extraction jar. Add small portions of the solutions at several sites on the surface of the soil or sediment.

11.1.2.3 Add 20 g of purified anhydrous sodium sulfate, and mix thoroughly using a stainless steel spoon or spatula.

11.1.2.4 Allow the mixture of soil and sodium sulfate to set for two hours at ambient temperature; mix again, break all visible lumps, and allow to set for at least four more hours.

11.1.2.5 Mix again and add 20 mL of methanol; mix again and add 150 mL of hexane.

11.1.2.6 Place the extraction jar containing the soil, sodium sulfate and solvents in the shaker and shake for at least 3 hours.

11.1.2.7 Remove the jar from the shaker and allow solids to settle. Decant the solvent through a glass funnel containing hexane-rinsed filter paper. Rinse the jar, solid sample residue, and filter residue with four 5-mL portions of hexane.

11.1.2.8 Concentrate the extract volume to approximately 2 to 3 mL with a Kuderna-Danish apparatus or a rotary evaporator. NOTE: Glassware used for more than one sample must be carefully cleaned between samples to prevent cross contamination (See Section 6.5).

11.1.2.9 Transfer the concentrated extract to an 8-mL glass culture tube. Rinse the evaporator flask with three 5-mL portions of hexane; transfer each rinse to the culture tube. Between additions of hexane rinse, reduce the extract volume in the culture tube enough to allow addition of another 5-mL volume of rinse. To reduce the volume, place the culture tube in a water bath adjusted to operate at 50°C and position the tube so that the surfaces of the extract and the water are at about the same level. Evaporate the solvent with a stream of nitrogen (flow rate of approximately 150 mL/min) with the tip of the nitrogen delivery tube 2 cm above the solution.

11.1.2.10 After the final rinse has been added, reduce the extract volume to approximately 1 mL.

11.2 Column Chromatography

11.2.1 Column Preparation

11.2.1.1 Column 1: Place 1.0 g of silica gel into a 1 cm x 20 cm column and tap the column gently to settle the silica gel. Add 2 g sodium hydroxideimpregnated silica gel, 1 g silica gel, 4.0 g of sulfuric acid-impregnated silica gel, and 2 g silica gel. Tap column gently after each addition.

11.2.1.2 Column 2: Place 6.0 g of alumina into a 1 cm x 30 cm column and tap the column gently to settle the alumina. Add a 1-cm layer of purified sodium sulfate to the top of the alumina.

11.2.1.3 Add hexane to each column until the packing is free of channels and air bubbles. A small positive pressure (5 psi) of clean nitrogen can be used if needed.

11.2.2 Quantitatively transfer the hexane sample extract from the culture tube to the top of the sulfuric acid-impregnated silica gel in Column 1. Rinse the culture tube with two 0.5 mL portions of hexane; transfer rinses to Column 1.

11.2.3 With 90 mL of hexane, elute the extract from Column 1 directly into Column 2 containing alumina and sodium sulfate.

11.2.4 Add 20 mL of hexane to Column 2 and elute until the hexane level is just below the top of the sodium sulfate; discard the eluted hexane.

11.2.5 Add 20 mL of 20% methylene chloride/80% hexane (volume/volume) to Column 2 and collect the eluate.

11.2.6 Reduce the volume of eluate with a gentle stream of filtered dry nitrogen. When the volume is about 1 to 2 mL, transfer aliquots to a 1-mL amber mini-vial with conical reservoir. Concentrate and add additional aliquots with further concentration until entire eluate is transferred. Rinse eluate container with two 0.5-mL portions of hexane; transfer rinses to the mini-vial, with further concentration as necessary. CAUTION: Do not evaporate sample extract to dryness.

11.2.7 With the final sample extract volume at approximately 1 mL, store the extract until time for GC/MS analysis.

11.3 GC/MS Analysis

11.3.1 Remove the sample extract or blank from storage and allow it to warm to ambient laboratory temperature if necessary.

With a stream of dry, filtered nitrogen, reduce the extract/blank volume to near dryness. Immediately before GC/MS analysis, adjust the extract or blank volume to 50 $\mu$L with toluene.

11.3.2 Inject a 2-$\mu$L aliquot of the extract into the GC, operated under conditions previously used (Sect. 9) to produce acceptable results with the performance check solution.

11.3.3 Acquire mass spectral data for the following selected characteristic ions: m/z 257, 320, and 322 for unlabeled 2,3,7,8-TCDD; m/z 328 for $^{37}Cl_4$-2,3,7,8-TCDD; and m/z 332 and 334 for $^{13}C_{12}$-2,3,7,8-TCDD. Use the same data acquisition time and MS operating conditions previously used (Sect. 9.3.8) to determine response factors.

11.4 Identification Criteria. NOTE: Refer to Exhibit E, Section 7, for application of identification criteria.

11.4.1 Retention time (at maximum peak height) of the sample component must be within 3 seconds of the retention time of the $^{13}C_{12}$-2,3,7,8-TCDD. Retention times are required for all chromatograms, but scan numbers are optional. These parameters should be printed next to the appropriate peak.

11.4.2 The integrated ion currents detected for m/z 257, 320, and 322 must maximize simultaneously. If there are peaks that will affect the maximization or quantitation of peaks of interest, attempts should be made to narrow the scan window to eliminate the interfering peaks. This should be reported on a separate chromatogram.

11.4.3 The integrated ion current for each analyte and surrogate compound ion (m/z 257, 320, 322 and 328) must be at least 2.5 times background noise and must not have saturated the detector; internal standard ions (m/z 332 and 334) must be at least 10 times background and must not have saturated the detector.

11.4.4 Relative abundance of m/z 257 to m/z 322 should be $\geq$ 20% and $\leq$ 45%.

11.4.5 Abundance of integrated ion counts detected for m/z 320 must be $\geq$ 67% and $\leq$ 87% of integrated ion counts detected for m/z 322.

11.5 Column Chromatography Procedure for Difficult Samples -- Use the following procedure for extracts previously subjected to the column chromatography procedures in Section 11.2, but found by GC/MS analysis to contain interfering components.

11.5.1 Mix 3.6 grams of Carbopack C (or equivalent) with 16.4 grams of Celite 545$^{R}$ (or equivalent) in a 40-mL vial and activate by heating in an oven at 130°C for 6 hours. Store in a desiccator. CAUTION: Check each new batch of mixed Carbopack/Celite$^{R}$ to ensure TCDD recovery of $\geq$ 50%. Subject the low level concentration calibration solution to this procedure and measure the quantity of labeled and unlabeled 2,3,7,8-TCDD.

11.5.2 Insert a small plug of glass wool into a disposable pipet approximately 15 cm long by 7 mm O.D. Apply suction with a vacuum aspirator attached to the pointed end of the pipet, and add the Carbopack/Celite$^{R}$ mixture until a 2 cm column is obtained.

11.5.3 Pre-elute the column with:

11.5.3.1 2 mL of toluene

11.5.3.2 1 mL of a mixture of 75% (by volume) methylene chloride, 20% methanol and 5% benzene

11.5.3.3 1 mL of 50% (by volume) cyclohexane and 50% methylene chloride

11.5.3.4 2 mL of hexane

11.5.4 While the column is still wet with hexane, add the sample extract. Elute the column with the following sequence of solvents and discard eluents.

11.5.4.1 2 mL of hexane

11.5.4.2 1 mL of 50% (by volume) cyclohexane and 50% methylene chloride

11.5.4.3 1 mL of 75% (by volume) methylene chloride, 20% methanol and 5% benzene

11.5.5 Elute with 2 mL of toluene and collect the eluent, which contains the TCDD.

11.5.6 Store the sample extract until just before GC/MS analysis.

## 12. CALCULATIONS

### 12.1 Concentration

12.1.1 Concentration when a linear response factor was obtained:

12.1.1.1 Calculate the concentration of 2,3,7,8-TCDD using the formula:

$$C_x = \frac{A_x \cdot Q_{is}}{A_{is} \cdot RF \cdot W}$$

where $C_x$ = 2,3,7,8-TCDD concentration in micrograms per kilogram

$A_x$ = the sum of integrated ion abundance detected for m/z 320 and 322

$A_{is}$ = the sum of integrated ion abundances detected for m/z 332 and 334 (characteristic ions of $^{13}C_{12}$-2,3,7,8-TCDD, the internal standard)

$Q_{is}$ = quantity (in nanograms) of $^{13}C_{12}$-2,3,7,8-TCDD added to the sample before extraction

RF = calculated mean response factor for unlabeled 2,3,7,8-TCDD relative to $^{13}C_{12}$-2,3,7,8-TCDD

W = weight (in grams) of wet soil or sediment sample.

12.1.1.2 If the calculated concentration of unlabeled 2,3,7,8-TCDD exceeds 200 μg/kg, which is the maximum concentration of the concentration calibration solutions, the linear range may have been exceeded, and a smaller aliquot of that sample must be analyzed. Accurately weigh to three significant figures a 1-g aliquot of the wet soil/sediment. Add 100 μL of the sample fortification solution (Section 7.8), just as for the larger sample aliquot. Extract and analyze.

12.1.1.3 Calculate the concentration of the surrogate compound, $^{37}Cl_4$-2,3,7,8-TCDD, using the formula:

$$C_s = \frac{A_s \cdot Q_{is}}{A_{is} \cdot RF \cdot W}$$

$C_s$ = concentration (in micrograms per kilogram) of the surrogate compound

$A_s$ = total integrated ion abundance of m/z 328 after correction for the contribution by unlabeled 2,3,7,8-TCDD (correction -- subtract 0.9% of the total integrated ion abundance detected for m/z 322 in the same sample extract)

$A_{is}$ = the sum of integrated ion abundances detected for m/z 332 and 334 (characteristic ions of $^{13}C_{12}$-2,3,7,8-TCDD, the internal standard)

$Q_{is}$ = quantity (in nanograms) of $^{13}C_{12}$-2,3,7,8-TCDD added to the sample before extraction

RF = calculated mean response factor for $^{37}Cl_4$-2,3,7,8-TCDD relative to $^{13}C_{12}$-2,3,7,8-TCDD

W = weight (in grams) of wet soil or sediment sample.

12.2 Accuracy -- Calculate the accuracy (A) of the measurement of surrogate, $^{37}Cl_4$-2,3,7,8-TCDD, using the formula:

$$\text{Surrogate Percent Accuracy} = \frac{\text{amount measured (nanograms)}}{10 \text{ ng}} \times 100$$

12.3 Estimated Detection Limit -- For samples in which no unlabeled 2,3,7,8-TCDD was detected, calculate the estimated minimum detectable concentration, which is the concentration required to produce a signal with area (or peak height) of 2.5 times the background signal area (or peak height). The background area is determined by integrating ion abundances for either m/z 320 or 322 in the appropriate region of the SICP, multiplying that area by 2.5, and relating the product area to an estimated concentration that would produce that product area.

Use the formula:

$$C_E = \frac{2.5 \cdot A_x \cdot Q_{is}}{A_{is} \cdot RF \cdot W}$$

where $C_E$ = estimated concentration of unlabeled 2,3,7,8-TCDD required to produce $A_x$

$A_x$ = peak height or integrated ion abundance for either m/z 320 or 322 in the same group of $\geq$ 5 spectra used to measure $A_{is}$

$A_{is}$ = peak height or integrated ion abundance for the appropriate ion characteristic of the internal standard, m/z 332 when m/z 320 is used to determine $A_x$, and m/z 334 when m/z 322 is used to determine $A_x$

$Q_{is}$, RF, and W retain the definitions previously stated in Section 12.1.1.

The use of the area (or peak height) for m/z 320 to calculate $C_E$ is preferred to m/z 322, but m/z 322 can be used when interference is observed for m/z 320 but not for m/z 322.

NOTE: This calculation is not applicable to all samples in which 2,3,7,8-TCDD was not identified (see Section 12.4).

12.4 Estimated Maximum Possible Concentration -- For samples where interference is observed for both m/z 320 and 322 or when an unacceptable ratio prevented identification of unlabeled 2,3,7,8-TCDD as a sample component, the procedure in Section 12.1 can be used to estimate the maximum concentration that could be represented by detected signals.

12.5 The relative percent difference (RPD%) is calculated as follows: (See Section 5.1.1, Exhibit E.)

$$RPD = \frac{|S_1 - S_2|}{\text{Mean Concentration}} = \frac{|S_1 - S_2|}{\frac{S_1 + S_2}{2}}$$

$S_1$ and $S_2$ represent sample and duplicate sample results.

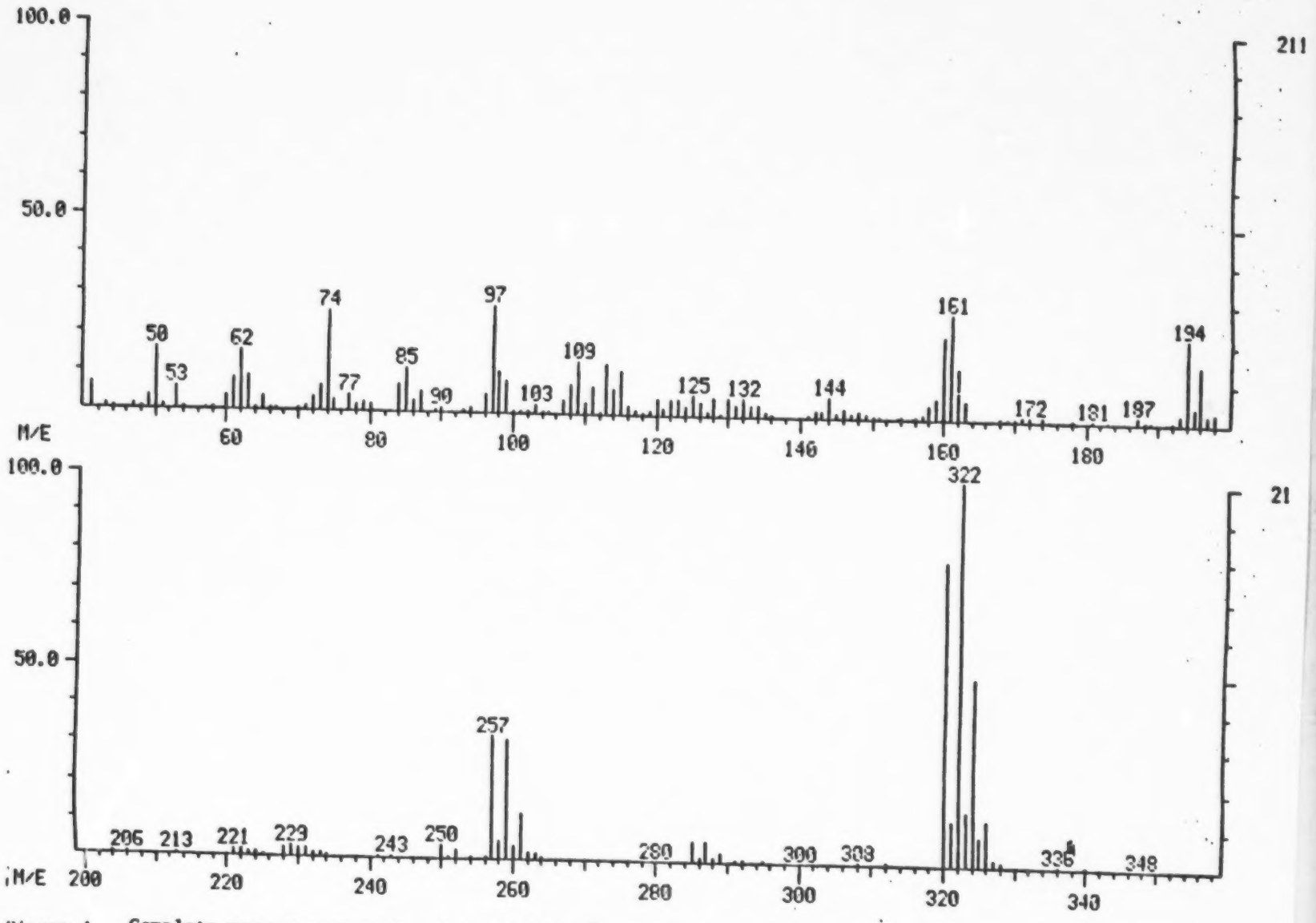


Figure 1. Complete mass spectrum of unlabeled 2,3,7,8-TCDD acquired with recommended GC conditions (Table 1).

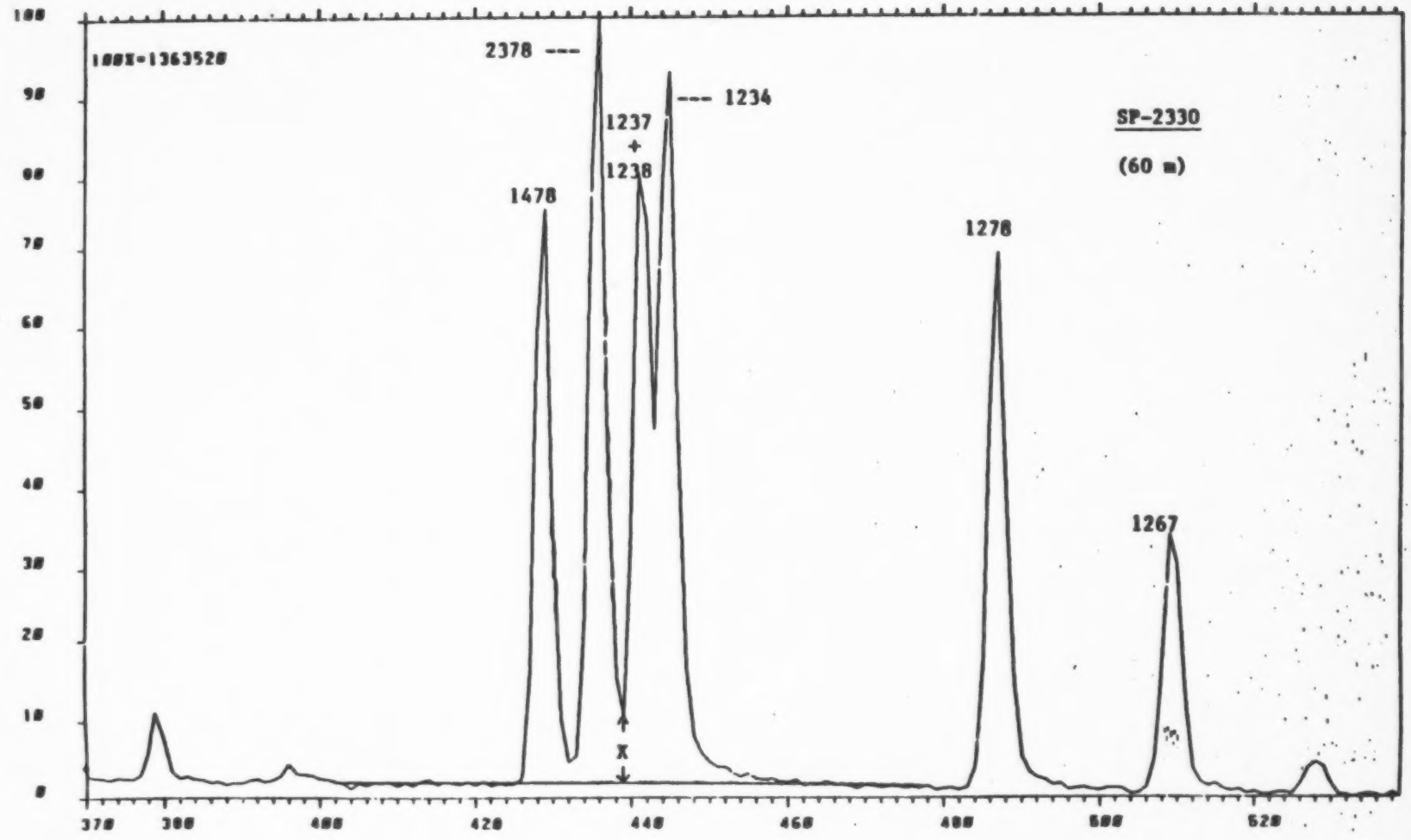


Figure 2. Selected ion current profile for m/z 320 and 322 produced by MS analysis of performance check solution using a 60-m SP-2330 fused silica capillary column and conditions listed in Table 1.

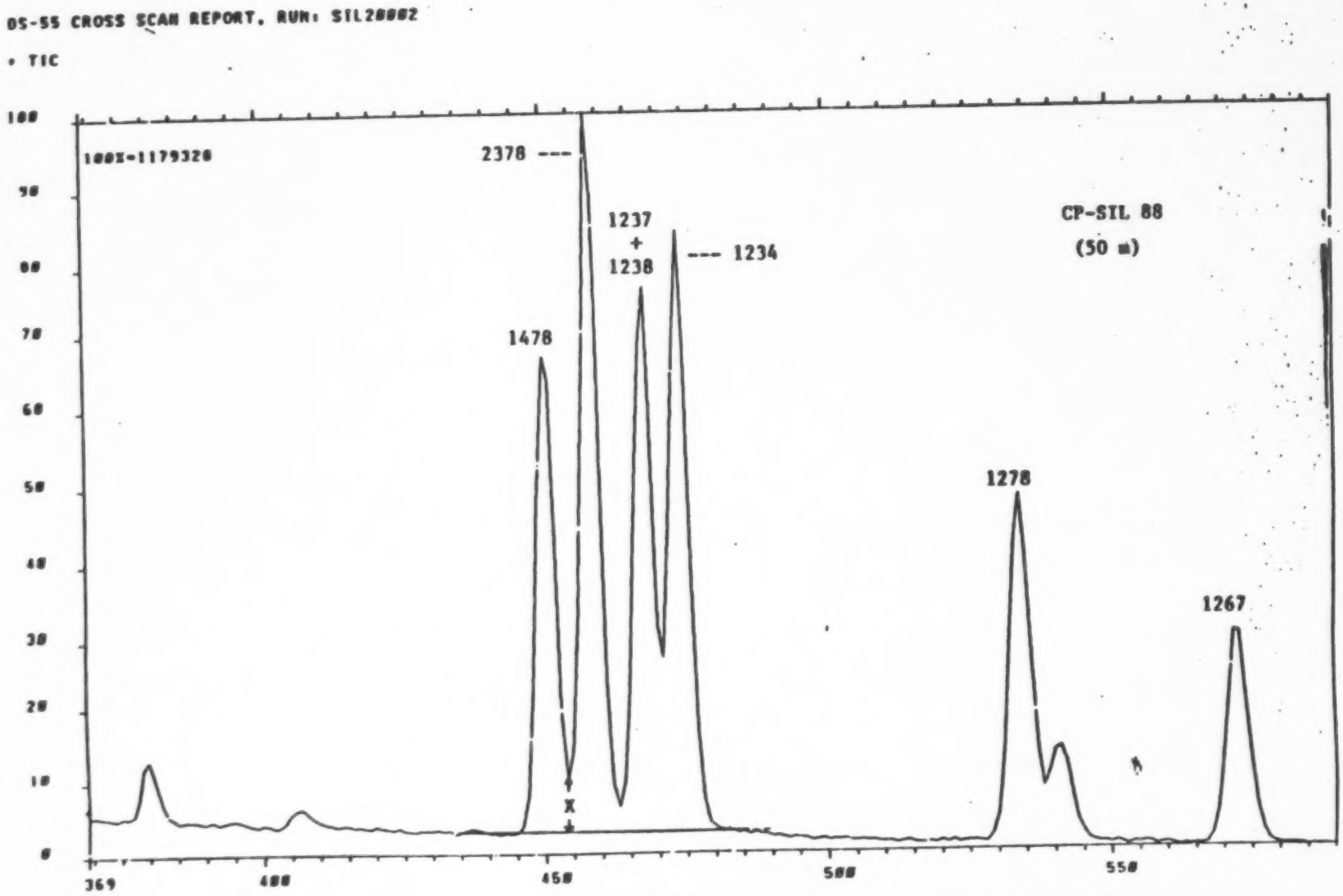


Figure 3. Selected ion current profile for m/z 320 and 322 produced by MS analysis of performance check solution using a 50-m CP-SIL 88 fused silica capillary column and conditions listed in Table 1.

TABLE 1. RECOMMENDED GC OPERATING CONDITIONS

| | | |
|---|---|---|
| Column coating | SP-2330 | CP-SIL 88 |
| Film thickness | 0.2 $\mu$m | 0.22 $\mu$m |
| Column dimensions | 60 m x 0.24 mm | 50 m x 0.22 mm |
| Helium* linear velocity | 28-29 cm/sec at 260°C | 28-29 cm/sec at 240°C |
| Initial temperature | 70°C | 45°C |
| Initial time | 4 min | 3 min |
| Temperature program | Rapid increase to 200°C<br>200°C to 260°C at 4°C/min | Rapid increase to 190°C<br>190°C to 240°C at 5°C/min |
| 2,3,7,8-TCDD retention time | 24 min | 26 min |

* Hydrogen is an acceptable carrier gas.

TABLE 2. COMPOSITION OF CONCENTRATION CALIBRATION SOLUTIONS

| Solution # | Concentration of 2,3,7,8-TCDD | | |
|---|---|---|---|
| | Isotopically Labeled | | Unlabeled |
| | $^{13}C_{12}$ | $^{37}Cl_4$ | |
| 1 | 1 ng/$\mu$L | 0.06 ng/$\mu$L | 0.2 ng/$\mu$L |
| 2 | 1 ng/$\mu$L | 0.12 ng/$\mu$L | 1 ng/$\mu$L |
| 3 | 1 ng/$\mu$L | 0.2 ng/$\mu$L | 5 ng/$\mu$L |
| 4 | 1 ng/$\mu$L | 0 | 20 ng/$\mu$L |
| 5 | 1 ng/$\mu$L | 0 | 40 ng/$\mu$L |

# APPENDIX C

# ANALYTICAL DATA TABLES

## APPENDIX C: SAMPLE DATA

### BATCHES 1 THROUGH 4

| Batch No. | ppb | Batch No. | ppb | Batch No. | ppb | Batch No. | ppb |
|---|---|---|---|---|---|---|---|
| DX000101 | 91.9 | DX000201 | 89.2 | DX000301 | | DX000401 | 64. |
| DX000102 | 110. | DX000202 | 93.8 | DX000302 | | DX000402 | 73. |
| DX000103 | 96.5 | DX000203 | 89.6 | DX000303 | | DX000403 | 99. |
| DX000104 | 96.9 | DX000204 | 89.2 | DX000304 | | DX000404 | 109. |
| DX000105 | 103. | DX000205 | 86.7 | DX000305 | 117. | DX000405 | 100. |
| DX000106 | 59.9 | DX000206 | 91.8 | DX000306 | 116. | DX000406 | 99.8 |
| DX000107 | 91.5 | DX000207 | 58.8 | DX000307 | 91.4 | DX000407 | 124. |
| DX000108 | 104. | DX000208 | 84.6 | DX000308 | 115. | DX000408 | 153. |
| DX000109 | 104. | DX000209 | 90.9 | DX000309 | 120. | DX000409 | 121. |
| DX000110 | 99.7 | DX000210 | 82.6 | DX000310 | 108. | DX000410 | 128. |
| DX000111 | 103. | DX000211 | 90.1 | DX000311 | 92.9 | DX000411 | 143. |
| DX000112 | 77.9 | DX000212 | 89.3 | DX000312 | | DX000412 | 127. |
| DX000113 | 97.9 | DX000213 | 83.0 | DX000313 | | DX000413 | 114. |
| DX000114 | 101. | DX000214 | 83.9 | DX000314 | | DX000414 | 95.8 |
| DX000115 | 97.1 | DX000215 | 89.6 | DX000315 | 76.9 | DX000415 | 127. |
| DX000116 | 93.9 | DX000216 | 90.1 | DX000316 | 65.5 | DX000416 | 56. |
| DX000117 | 93.9 | DX000217 | 94.5 | DX000317 | | DX000417 | 145. |
| DX000118 | 92.8 | DX000218 | 98.9 | DX000318 | | DX000418 | 99.2 |
| DX000119 | 1.1 | DX000219 | | DX000319 | | DX000419 | 117. |
| | | | | | | DX000420 | 3.9 |

"*" - not taken

## APPENDIX C: SAMPLE DATA (continued)

### BATCHES 5 THROUGH 8

| Batch No. | ppb | Batch No. | ppb | Batch No. | ppb | Batch No. | ppb |
|---|---|---|---|---|---|---|---|
| DX000501 | 57. | DX000601 | 106. | DX000701 | 96. | DX000801 | |
| DX000502 | 88. | DX000602 | 85. | DX000702 | 82. | DX000802 | |
| DX000503 | 112. | DX000603 | 96. | DX000703 | 94. | DX000803 | |
| DX000504 | 84. | DX000604 | 98. | DX000704 | 86. | DX000804 | |
| DX000505 | 97. | DX000605 | 127. | DX000705 | 72. | DX000805 | |
| DX000506 | 125. | DX000606 | 155. | DX000706 | 74. | DX000806 | |
| DX000507 | 133. | DX000607 | 107. | DX000707 | 86. | DX000807 | |
| DX000508 | 105. | DX000608 | 126. | DX000708 | 106. | DX000808 | |
| DX000509 | 103. | DX000609 | 127. | DX000709 | 61. | DX000809 | |
| DX000510 | 124. | DX000610 | 112. | DX000710 | 108. | DX000810 | |
| DX000511 | 87. | DX000611 | 120. | DX000711 | 103. | DX000811 | |
| DX000512 | 109. | DX000612 | 1.1 | DX000712 | 115. | DX000812 | |
| DX000513 | 110. | | | DX000713 | 84. | DX000813 | |
| DX000514 | 112. | | | DX000714 | 74. | DX000814 | |
| DX000515 | 91. | | | DX000715 | 92. | DX000815 | |
| DX000516 | 130. | | | DX000716 | 86. | DX000816 | |
| DX000517 | 121. | | | DX000717 | 77. | DX00817 | |
| DX000518 | 145. | | | DX000718 | 3.94 | DX000818 | 2.43 |
| DX000519 | 139. | | | | | | |
| DX000520 | 130. | | | | | | |
| DX000521 | 3. | | | | | | |
| DX000522 | 238. | | | | | | |
| DX000523 | 264. | | | | | | |
| DX000524 | 320. | | | | | | |

## APPENDIX C: SAMPLE DATA (continued)

### BATCHES 9 THROUGH 12

| Batch No. | ppb | Batch No. | ppb | Batch No. | ppb | Batch No. | ppb |
|---|---|---|---|---|---|---|---|
| DX000901 | 128. | DX001001 | 94. | DX001101 | | DX001201 | 95. |
| DX000902 | 113. | DX001002 | 88. | DX001102 | | DX001202 | 94. |
| DX000903 | 119. | DX001003 | 109. | DX001103 | | DX001203 | 121. |
| DX000904 | 91. | DX001004 | 65. | DX001104 | | DX001204 | 65. |
| DX000905 | (642) | DX001005 | 95. | DX001105 | | DX001205 | 95. |
| DX000906 | 133. | DX001006 | 74. | DX001106 | | DX001206 | 143. |
| DX000907 | 104. | DX001007 | 64. | DX001107 | | DX001207 | 186. |
| DX000908 | 82. | DX001008 | 112. | DX001108 | | DX001208 | 70. |
| DX000909 | 105. | DX001009 | 86. | DX001109 | | DX001209 | 149. |
| DX000910 | 129. | DX001010 | 127. | DX001110 | | DX001210 | 86. |
| DX000911 | 144. | DX001011 | 114. | DX001111 | 66. | DX001211 | 148. |
| DX000912 | 101. | DX001012 | 117. | DX001112 | | DX001212 | -- |
| DX000913 | 14.6 | DX001013 | 59. | DX001113 | 53. | DX001213 | ND |
| DX000914 | 73.3 | DX001014 | 68. | DX001114 | 100. | DX001214 | ND |
| DX000915 | 143. | DX001015 | 97. | DX001115 | | DX001215 | 0.3 |
| DX000916 | 69.1 | DX001016 | 58. | DX001116 | 108. | DX001216 | 64. |
| DX000917 | 1.2 | DX001017 | 56. | DX001117 | | DX001217 | 44. |
| DX000918 | (511) | DX001018 | 82. | DX001118 | | DX001218 | 2.2 |
| DX000919 | 10.7 | DX001019 | 103. | DX001119 | | DX001219 | 1.8 |
| DX000920 | 3.4 | DX001020 | .98 | DX001120 | | DX001220 | .65 |